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# ON SOME DOUBLE HALIDES OF MERCURY.

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## *Introduction.*

In continuation of the investigations which have been in progress for some years in this laboratory on the so-called double halides, work was begun on the compounds which mercuric chloride forms with the chlorides of the other elements of the second group of the Periodic System. After some months of work upon these, attention was turned to the possibility of forming double salts with the salts of organic bases like aniline and the toluidines; and the following work was done on these compounds. On account of the more satisfactory results of this work arising from the greater ease of formation and purification of the compounds formed, the description of these will be given first,—the description of the inorganic mercurates being left for the latter part of the paper.

## *Historical.*

Some double halides of metals with the halides of aromatic organic bases have been prepared and described. Destrem[2] prepared an aniline chlorocuprate, $CuCl_2 2(C_6H_5NH_3Cl)$, by adding aniline hydrochloride to an alcoholic solution of cupric chloride. This he describes as a well-behaved salt.

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[1] From the Author's Dissertation submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1893. The work was undertaken at the suggestion of Professor Remsen, and carried on under his guidance.

[2] Bull. Soc. Chim., **30**, 482.

Bibanow[1] prepared an orthotoluidine chlorozincate, $(C_7H_7NH_3Cl)_2ZnCl_2$, by bringing together a concentrated solution of zinc chloride and orthotoluidine hydrochloride, and crystallizing at a temperature of —5°.

Widmann[2] described a metatoluidine chloroplatinate, $(C_7H_7NH_3Cl)_2PtCl_4$. These salts are also described:

$(C_7H_7NH_3Cl)_2ZnCl_2(p)$;[3] $(C_6H_5NH_3Cl)_2SnCl_4$;[4]
$(C_7H_7NH_3Cl)_2SnCl_4$;[4] and $(C_7H_7NH_3Cl)PtCl_4$.[5]

The platinum salt, $C_6H_5NH_3Cl.PtCl_4$, was made by Hofmann[6] by bringing together aniline, hydrochloric acid, and platinic chloride. After describing this salt he attempted to make a mercury salt, but did not proceed in the same manner, and therefore got a salt of a different nature; *viz.*, aniline mercuric chloride ("Kyanolquecksilberchlorid"). In speaking of the properties of this he says: "Auch von Chlorwasserstoffsäure wird es gelöst. Hat man zu wenig Salzsäure zugesetzt, so schmilzt der ungelöste Theil beim Erwärmen zu einem rothen Oele, welches den Boden der Röhre bedeckt. Durch Zusatz von mehr Salzsäure erhält man aber wieder eine klare Lösung aus der sich beim Erkalten schöne weisse Krystalle absetzen. Ich weiss nicht ob diess die unveränderte Quecksilberverbindung ist oder ob Chlorwasserstoffsäure in die Zusammensetzung aufgenommen wurde."

The corresponding iodides, bromides, and cyanides of mercury and other metals are described in a few instances; *e.g.*,

$BiI_3C_6H_5NH_3I$;[7] and $Hg(CN)_2C_6H_5NH_3CN$.[8]

No investigation seems to have been made with the idea of preparing two or more series of salts with the same metal, such, *e. g.*, as $C_6H_5NH_3ClM''Cl_2$, $C_6H_5NH_3Cl2M''Cl_2$, etc. The salts were made by simply bringing solutions together with no particular care as to proportions so that a precipitate was formed immediately or on cooling. Of course at the time this work was done there was no incentive for making any investigations of this kind. It was simply an open field and no classification was attempted, the only generalization being, "it has the power to form double salts."

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[1] Jsb. Chem., 1874, 747.

[2] Ber. d. chem. Ges., **13**, 677.

[3] Gräfinghoff: Ztschr. Chem., 1865, 599.

[4] Hjortdahl: Ztschr. Kryst., **6**, 490.

[5] Muspratt, Hofmann: Ann. Chem. (Liebig), **54**, 16.

[6] Ann. Chem. (Liebig), **47**, 62.

[7] Kraut: *Ibid.*, **210**, 323.

[8] Claus u. Merck: Ber. d. chem. Ges., **16**, 2737.

Wells[1] describes a new class of double salts of the general formula $M'_3M''Hl_5$ or $3M'Hl, M''Hl_2$. Although, judging from the analyses given, he did not succeed in preparing very pure specimens of these salts, yet the crystallographic description given by Penfield taken with the description of the salts indicates their reality. The difficulty of the preparation of pure specimens and their recrystallization from a solvent has interfered with the investigation of the possibility of the preparation of salts of this class and other classes, such as $4M'Hl.M''Hl_2$, etc.

The present class of compounds seemed to be free from this great difficulty to a large degree, and therefore strenuous efforts were made to prepare compounds of the above classes, but in all cases without success, as will be shown later. This is no argument, however, against the existence of such compounds, because these bases vary among themselves as to the classes of compounds formed. This fact gave rise to a great deal of work in the endeavor to get uniform classes of salts with each base. Another question of interest at this time in this line of work is in regard to the possibility of the formation of mixed double halides. Can a salt like $M'M''(Cl)_2Br$ or $M'M''(ClBr)Cl$ exist? Wells[2] has shown the existence of compounds like $Cs(Cl)_2Br$, and used Remsen's hypothesis in their explanation; *viz.*, that two halogen atoms play the part of an oxygen atom. He is led to the conclusion that this couplet can consist of different atoms. In the article above cited[3] Wells describes the preparation of mixed double halides. Here again the difficulty of procuring definite products interfered with the exactness in results which one might desire, but there seems to be good evidence of the existence of these salts.

[1] Am. J. Sci., **44**, 222.

[2] *Ibid.*, **43**, 31.

[3] *Loc. cit.*

Before this work, Atkinson had described these salts :[1]

$K_3SbCl_3Br_3 12H_2O$; and $SbCl_3BrKH_2O$.

Pitkins[2] described the salt $2KBr.PtCl_4$. Remsen and Richardson,[3] working with potassium-tin salts, were led to the conclusion that the existence of a pure mixed salt of potassium and tin was doubtful. Later, Herty described his fruitless endeavors to prepare mixed double halides with lead and potassium.

During the time that the work on the chlorides about to be described was in progress, work was prosecuted on the attempt to prepare mixed halides. Mercuric bromide was used with the chlorides of the organic bases in each case. Many crops of crystals were obtained—sometimes three sets of them in the same beaker, and for some time it seemed a hopeless task to attempt to get anything definite, but, after many failures, some uniform crops of crystals were obtained at last, and these proved to be mixed double halides.

The following salts are described in this paper :

*Aniline Salts.*

$C_6H_5NH_3Hg_2Cl_5$.
$C_6H_5NH_3HgCl_3$.
$(C_6H_5NH_3)_2HgCl_4$.

*Orthotoluidine Salts.*

$C_7H_7NH_3Hg_2Cl_5$.
$C_7H_7NH_3HgCl_3$.
$(C_7H_7NH_3)_2HgCl_4$.

*Metatoluidine Salts.*

$C_7H_7NH_3Hg_2Cl_5$.
$C_7H_7NH_3HgCl_3$.
$(C_7H_7NH_3)_2HgCl_4$.

*Paratoluidine Salt.*

$C_7H_7NH_3HgCl_3$.

*Mixed Salt.*

$C_7H_7NH_3HgBr_2Cl$.

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[1] J. Chem. Soc. (London), **43**, (1883), 289.

[2] Chem. News, **47**, 118.

[3] This JOURNAL, **14**, 96.

[4] *Ibid.*, **15**, 81.

*Inorganic Salts.*

$MgHg_3Cl_8 + 6H_2O$.

$SrHg_3Cl_8 + (H_2O)x$.

$BaHg_3Cl_8 + 8H_2O$.

It will be noticed that among the organic salts the class $BHClHgCl_2$ is the only one found with all four bases—the classes $BHCl.2HgCl_2$ and $2BHCl.HgCl_2$ being found with all except paratoluidine (B being used to represent a base, as aniline).

*Naming of Compounds.*—No complete system of naming the double halides has yet been adopted. The first and second aniline salts are easily named; thus, Dianiline chloromercurate, and aniline chloromercurate. The third might be called aniline dichloromercurate, or aniline chlorodimercurate. In this paper the former will be used and the analogous names in case of the toluidine salts.

*Methods of Analysis.*—In making analyses of these salts only chlorine and mercury were determined. The estimation of mercury was made by precipitation as sulphide. This required some time for complete precipitation as sulphide, owing to the fact that a yellow, or yellowish white precipitate of sulphochloride is first formed, and care must be taken to have this completely changed to the sulphide. Some free sulphur is sometimes precipitated, but this can usually be dissolved by washing the precipitate with alcohol and then with carbon bisulphide. In making mercury determinations the solutions were acidified with hydrochloric acid. The filters used were washed, dried, and weighed before using, and then the precipitate was weighed on the filter, and the weight of the latter deducted. Satisfactory results were obtained by this method with pure mercuric chloride as a test of the method. Some of the determinations were made in a Gooch crucible. The drying of the precipitate was conducted in an air-bath kept near 90°. Greater difficulty was experienced in getting a satisfactory method for the estimation of chlorine. Owing to the fact that it cannot be estimated in presence of mercuric chloride,[1] it was necessary to remove the latter. This was done with hydrogen sulphide. Then the problem of getting out the excess of the latter was to be solved, as it could not be driven off by heat for fear of losing some hydrochloric acid at the same time. After trying several methods it was finally removed as free sulphur by the addition of ammonium ferric alum to the solution, letting it stand for several hours, and filtering. Chlorine was then precipitated as silver chloride, and weighed in a Gooch crucible. In some of the work on the inorganic salts, chlorine was estimated volumetrically, but the gravimetric method gave more satisfactory results. The salts for analysis were purified by treatment with animal charcoal, and recrystallization from water acidified with hydrochloric acid.

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[1] See Fresenius' Quant. Analyse, 1, 473.

## ANILINE SALTS.

*Aniline Dichloromercurate*, $C_6H_5NH_3Hg_2Cl_5$. — Following Destrem's method, aniline hydrochloride was added to an alcoholic solution of mercuric chloride. A salt was formed in irregular crystals while the solution became much colored and some kind of decomposition had evidently taken place which interfered with the purity of the product. The same experiment was performed, using a water solution instead of alcohol. 9 grams of aniline hydrochloride were dissolved in warm water, 20 grams of mercuric chloride were added, and the whole heated and filtered. A salt began to crystallize almost at once. This salt was freed from the mother-liquor and washed with water on the filter-pump. The salt which was formed in alcohol was recrystallized from hot water. Determinations of mercury in both indicated the came compound; *viz.*, Aniline dichloromercurate, $C_6H_5NH_3Hg_2Cl_5$. In the meantime work on the water solutions, which will be described later in connection with the paratoluidine salt, was done, and solutions acidified with hydrochloric acid were used after this. Following these suggestions, aniline hydrochloride and mercuric chloride were mixed in a beaker in molecular quantities for the above salt; then water and a little hydrochloric acid added, and the whole heated to boiling. A beautiful white salt, in sheaves, sometimes in rosettes, crystallized on cooling. The salt was well washed with cold water on the filter-pump and recrystallized from acidified water solution after treatment with animal charcoal. The salt was analyzed for mercury and chlorine with the following results:

I. 0.6727 gram salt gave 0.4651 gram HgS.
II. 0.4727 gram salt gave 0.3263 gram HgS.
III. 0.7735 gram salt gave 0.8307 gram AgCl.
IV. 0.8180 gram salt gave 0.8784 gram AgCl.

| | Calculated for $C_6H_5NH_3Hg_2Cl_5$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Hg | 59.62 | 59.60 | 59.51 | .... | .... |
| Cl | 26.38 | .... | .... | 26.56 | 26.55 |

In the first preparation the salt was formed when the aniline hydrochloride was in excess, and the solution boiled. Repeated trials showed that the best results were obtained when mercuric chloride was present in slight excess.

*Properties.*—Aniline dichloromercurate is much more readily soluble in hot than cold water, being rather insoluble in the latter. It is much more soluble in methyl and ethyl alcohols. It is only slightly soluble in ether. When boiled for some time with alcohol it is decomposed to some extent. Heating to boiling in pure water does not decompose it. The salt is stable in the air if dry, but becomes discolored like many aniline salts if exposed for some time in moist condition.

*Aniline Chloromercurate*, $C_6H_5NH_3HgCl_3$.—Having obtained this aniline compound in the above manner, the attempt to prepare compounds having a larger, and those having a smaller, proportion of mercuric chloride was next in order. With this end in view, a larger proportion of mercuric chloride was added to constant quantities of aniline hydrochloride. This was carried on until the mercuric chloride would crystallize out with the salt described, and no compound containing a larger proportion of mercuric chloride was obtained. Gradually diminishing the proportion of mercuric chloride, a salt differing from the above was obtained, when molecular quantities of the chlorides were mixed and the solution not heated too strongly. It was found, however, that there was a tendency to pass into the first form when the solution of equal molecular quantities was boiled. By using a slight excess of aniline hydrochloride the new salt was obtained in better form. The salt was recrystallized from acidified water solution, washed with water on the filter-pump, and dried.

The analyses for mercury and chlorine of the purified salt gave the following results:

I. 0.7509 gram salt gave 0.4365 gram HgS.
II. 0.9662 gram salt gave 0.5585 gram HgS.
III. 0.5662 gram salt gave 0.6114 gram AgCl.
IV. 0.7075 gram salt gave 0.7604 gram AgCl.

| | Calculated for $C_6H_5NH_3HgCl_3$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Hg | 49.98 | 50.11 | 49.83 | .... | .... |
| Cl | 26.54 | .... | .... | 26.70 | 26.58 |

This salt was obtained from ethyl alcohol and from methyl alcohol solutions just as from water solutions. In all cases a small quantity of hydrochloric acid was added. Attempts were made to get better results and larger crystals by using the alcohols and allowing the solutions to evaporate gradually, but with only partial success. The solutions in all cases, except one with methyl alcohol, became very much discolored, and a green substance was continually being formed. This was often filtered off, and the solution cleared by animal charcoal, but only impure crystals were obtained, where they were obtained at all. The crystals seem to have the same general form, whether obtained from water or alcohol solutions.

*Dianiline Chloromercurate*, $(C_6H_5NH_3)_2HgCl_4$.—By using still smaller proportions of mercuric chloride to constant quantities of aniline hydrochloride, a third salt was obtained with a distinct crystalline form. This salt crystallized in bright glistening needles. It is much more soluble in water and dilute acid than the other salts, and for this reason could not be washed as easily without dissolving considerable of the salt, but it was recrystallized.

Analyses gave the following results:

I. 0.4696 gram salt gave 0.2058 gram HgS.
II. 0.7722 gram salt gave 0.8348 gram AgCl.
III. 0.6849 gram salt gave 0.7373 gram AgCl.

| | Calculated for $(C_6H_5NH_3)_2HgCl_4$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Hg | 37.77 | 37.78 | .... | .... |
| Cl | 26.75 | .... | 26.73 | 26.62 |

The salt is obtained most readily and without danger of the salt with more mercuric chloride being formed, if aniline hydrochloride is added in excess to the original solution.

*Properties.*—Dianiline chloromercurate is much more soluble than either of the above described chloromercurates. Concentrated solutions must be used in its preparation. By addition of the proper amount of mercuric chloride and boiling, it can be converted into aniline chloromercurate.

The process of adding a larger proportion of aniline hydrochloride was continued still further in different proportions, but no other compound was obtained. This last-described salt was always formed and then aniline hydrochloride would crystallize out mixed with the crystals of the salt. Repeated attempts with varying conditions of temperature, dilution, acidification, and proportions of ingredients gave the same results. We conclude that a salt with a larger proportion of aniline hydrochloride than is found in dianiline chloromercurate cannot be made by this method. No other method was tried. It was noted sometimes in the heating of the solutions from which the above salts crystallized, and always when they were slowly evaporated by heat, that a flocculent green substance was formed in the solution. This floated about and had to be separated by filtration. Owing to lack of time this has not been investigated, and the exact conditions suited to its formation were not learned. It was usually much more abundant in the alcoholic solutions. It was observed that the salts with smaller proportions of mercuric chloride can be converted into those with larger proportions. On the other hand, the latter can be converted into the former by the addition of aniline hydrochloride. This is not as easily accomplished, however, and the aniline chloride must be added in excess and the solution boiled longer. Aniline dichloromercurate seems to be the salt most easily formed.

The mother-liquors from which these salts crystallized were slowly evaporated to learn if salts of different composition could be formed, but nothing new was found in this way. Sometimes a second crop of crystals of the salt first formed was obtained, but usually mixtures of the salts, or of the salts and the simple chlorides were formed.

### ORTHOTOLUIDINE SALTS.

*Orthotoluidine Dichloromercurate*, $C_7H_7NH_3Hg_2Cl_5$.—Following the indications of the experience with the aniline salts, nearly molecular quantities, for the above formula, of orthotoluidine hydrochloride and mercuric chloride were brought together in acidulated water solution, with the mercuric chloride in slight excess. A salt crystallized out on cooling. The first part of the crystallization was in irregular, ragged plates, and on top of these a few needles of prism-like crystals were deposited during the night. The two sets of crystals having apparently different solubilities, water was added, the solution heated and allowed to crystallize again, but with the same result. A new solution was made and it acted in the same way. One of these solutions was heated and the ragged crystals were again deposited on cooling. The mother-liquor was poured off and the crystals were washed with the aid of the filter-pump. The mother-liquor after a time began to form the prism-like crystals. These were also separated and washed. Estimations of mercury in the two salts indicated that both had the same composition; *viz.*, $C_7H_7NH_3Hg_2Cl_5$. Thinking the different forms of crystals were due to some impurity—possibly some para salt present,—a new start was made. The orthotoluidine first used was marked C. P. Some more of this was taken and treated with oxalic acid, and then by crystallization separated from any possible para salt present. The oxalate was then treated with a base and redistilled with steam. By this means a pure base was obtained and by treatment with pure hydrochloric acid and recrystallization, a most beautiful salt was obtained. On making the double salt, using this chloride, the crystals were deposited in beautiful leaf-like forms in which the veins extended beyond the border, giving a ragged edge. This was the general form first observed. There semed to be no tendency to form the other crystals in this case. The salt was then recrystallized and analyzed with the following results:

I. 0.5973 gram salt gave 0.4054 gram HgS.
II. 0.6948 gram salt gave 0.4703 gram HgS.
III. 0.6740 gram salt gave 0.7096 gram AgCl.
IV. 0.9160 gram salt gave 0.9663 gram AgCl.

| | Calculated for $C_7H_7NH_3Hg_2Cl_5$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Hg | 58.40 | 58.51 | 58.35 | .... | .... |
| Cl | 25.85 | .... | .... | 26.04 | 26.09 |

*Orthotoluidine Chloromercurate*, $C_7H_7NH_3HgCl_3$.—Several attempts to make the above were, at first, unsuccessful. In fact, it was at first obtained by evaporating the mother-liquor from a crystallization of orthotoluidine dichloromercurate in which the organic chloride was in excess. By using a slight excess of the toluidine chloride, and only heating to the boiling-point, the salt was obtained.

Analyses of the purified salt gave these results:

I. 0.5802 gram salt gave 0.3247 gram HgS.
II. 0.5724 gram salt gave 0.3194 gram HgS.
III. 0.7748 gram salt gave 0.8111 gram AgCl.
IV. 0.6999 gram salt gave 0.7313 gram AgCl.

| | Calculated for $C_7H_7NH_3HgCl_3$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Hg | 48.30 | 48.24 | 48.10 | .... | .... |
| Cl | 25.65 | .... | .... | 25.89 | 25.84 |

*Properties.*—As regards its solubility and general properties this salt is very much like the corresponding aniline salt.

*Diorthotoluidine Chloromercurate*, $(C_7H_7NH_3)_2HgCl_4$.—This salt was readily formed by bringing the ingredients together in about the calculated proportions for the formation of the salt, but with the organic chloride in slight excess. A *small* amount of acidulated water must be used as the salt is quite soluble in cold water. It is not so readily purified as the others on account of the fact that it is so soluble as to preclude much washing. The salt crystallizes in bright, glistening needles or prisms, which are usually collected in rosettes. It is quite soluble in alcohol, and soon colors the solution on heating, showing decomposition. This is characteristic of the chlorides of the formula $(BH)_2HgCl_4$. They seem less stable than the halides with a larger proportion of mercuric chloride.

Analyses of the purified salt gave :

I. 0.5552 gram salt gave 0.2333 gram HgS.
II. 0.6308 gram salt gave 0.2637 gram HgS.
III. 0.4591 gram salt gave 0.4780 gram AgCl.
IV. 0.5974 gram salt gave 0.6169 gram AgCl.

| | Calculated for $(C_7H_7NH_3)_2HgCl_4$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Hg | 35.88 | 36.22 | 36.04 | .... | .... |
| Cl | 25.41 | .... | .... | 25.75 | 25.54 |

The properties of the orthotoluidine salts are much like those of the corresponding aniline salts. The intermediate salts are more difficult of preparation than the others, because of the ease with which they pass into the salt with more mercury on the one hand, and the liability of the formation of some of the salt with a less amount of mercury on the other. As in the case of the aniline salts, the toluidine salts become discolored on standing only a short time in solution. In the formation of dianiline chloromercurate and diorthotoluidine mercurate, particularly, is this the case. With these the flocculent green substance before mentioned was most abundant. As before, attempts were made to get a salt with a larger proportion of the organic chloride, but without success, although many efforts were made. There were no indications of a fourth salt in any case. Some beautiful six-sided plates were often formed, but these always proved to be pure orthotoluidine hydrochloride.

## METATOLUIDINE SALTS.

*Metatoluidine Dichloromercurate*, $C_7H_7NH_3Hg_2Cl_5$. — The above salt was readily obtained in the same manner as the corresponding salts already described. It was purified in the usual manner and analyzed with these results :

I. 0.4198 gram salt gave 0.2856 gram HgS.
II. 0.5938 gram salt gave 0.4027 gram HgS.
III. 0.4954 gram salt gave 0.5207 gram AgCl.
IV. 0.4874 gram salt gave 0.5119 gram AgCl.

| | Calculated for $C_7H_7NH_3Hg_2Cl_5$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Hg | 58.40 | 58.65 | 58.46 | .... | .... |
| Cl | 25.85 | .... | .... | 25.99 | 25.97 |

*Properties.*—Metatoluidine dichloromercurate crystallizes in thin plates or scales. It is very much like the corresponding aniline and orthotoluidine salts in solubility and other properties. The meta salt seems less soluble than the others. The crystallization took place soon after the solution began to cool—a certain temperature, rather than a certain concentration of solution, seeming to determine the point of saturation. The salt would all crystallize near this temperature. This was true of solutions of quite different concentration.

*Metatoluidine Chloromercurate*, $C_7H_7NH_3HgCl_3$. — The amount of metatoluidine at hand did not permit of as thorough an investigation of this salt as was given to those before described. This intermediate salt is the only one which suffered, however, from lack of material. It is the most difficult to get, and therefore required more of the ingredients used. One or two crops of crystals were obtained in small quantity, which had a satisfactory appearance. They were not recrystallized, however, and the analyses below are of the specimens of these crystallizations. The crystals which had a light-purplish color (probably due to impurities) formed in very thin plates which reached across the beaker, and broke up into scales when taken out.

Analyses of the specimen gave the following results :

I. 0.4126 gram salt gave 0.2289 gram HgS.
II. 0.4906 gram salt gave 0.2737 gram HgS.
III. 0.5730 gram salt gave 0.6031 gram AgCl.
IV. 0.6486 gram salt gave 0.6774 gram AgCl.

| | Calculated for $C_7H_7NH_3HgCl_3$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Hg | 48.30 | 47.82 | 48.13 | .... | .... |
| Cl | 25.65 | .... | .... | 26.03 | 25.83 |

*Dimetatoluidine Chloromercurate*, $(C_7H_7NH_3)_2HgCl_4$.—This salt was made in the usual way. It crystallized in thin glistening scales with grayish luster. Little need be said of it as it closely resembles the corresponding salts already described.

Analyses of the purified salt gave these results :

I. 0.4316 gram salt gave 0.1801 gram HgS.
II. 0.5152 gram salt gave 0.2147 gram HgS.
III. 0.4844 gram salt gave 0.5004 gram AgCl.
IV. 0.4851 gram salt gave 0.5002 gram AgCl.

| | Calculated for $(C_7H_7NH_3)_2HgCl_4$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Hg | 35.88 | 35.97 | 35.92 | .... | .... |
| Cl | 25.41 | .... | .... | 25.55 | 25.55 |

*Paratoluidine Chloromercurate*, $C_7H_7NH_3HgCl_3$. — About equimolecular quantities of the two chlorides were weighed into a beaker and water added. On heating gradually, a salt suddenly separated out which completely filled the space occupied by the liquid. This was dissolved on further heating, and the salt crystallized out on cooling. As there was some doubt as to the homogeneousness of the deposit, much more water was added, and a second crystallization was made. This appeared to give two sets of crystals, one more soluble than the other.

By adding more water and watching the process of separation of the crystals, the less soluble salt was obtained. A determination of mercury indicated the salt $C_7H_7NH_3HgCl_3$. Other trials seemed to indicate that a pure uniform salt could not be obtained with water alone. It either decomposed the salt formed or caused the action to proceed in such a manner as to form more than one salt. It was here found that, if the solutions were acidified with hydrochloric acid, uniform crystallizations could be obtained. Following the suggestion of these experiences, the salt was made by bringing together molecular quantities of paratoluidine hydrochloride and mercuric chloride. Water and a little hydrochloric acid were added and the whole gently heated. In a few minutes a precipitate was formed which filled the whole solution. On heating higher this dissolved, and readily crystallized on cooling in beautiful white needles. The needles were usually collected into sheaves or rosettes, but were sometimes alone. The salt was usually colored, unless the solution was treated with charcoal before crystallizing.

Analyses of the purified compound were made with the following results:

I. 0.7092 gram salt gave 0.3987 gram HgS.
II. 0.2581 gram salt gave 0.1454 gram HgS.
III. 0.6195 gram salt gave 0.6456 gram AgCl.
IV. 0.6567 gram salt gave 0.6867 gram AgCl.

| | Calculated for $C_7H_7NH_3HgCl_3$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Hg | 48.30 | 48.46 | 48.56 | .... | .... |
| Cl | 25.65 | .... | .... | 25.77 | 25.86 |

*Properties.*—Paratoluidine chloromercurate is much more soluble in hot than cold water, and can, therefore, be readily crystallized. It is more easily soluble in methyl and ethyl alcohols, but is insoluble in ether. The salt can be washed very thoroughly with cold water on the filter-pump, and this method was used. It was dried by pressing between layers of drying-paper. By crystallizing slowly, beautiful needles, nearly three inches long, were obtained. On exposure for a little time in the air of the laboratory in a moist condition, they assume a rose tint, and become more discolored on longer standing. When thoroughly dried they assume a very slight brownish or cream tint on standing in a weighing-tube.

Next, a solution of the original chlorides in the proportion of one molecule of paratoluidine hydrochloride to two of mercuric chloride was made, when the same salt was obtained. This solution was boiled for some time, and solutions with this proportion of chlorides, and with varying amounts of hydrochloric acid were made, but the same results were always obtained. A salt of the composition $C_7H_7NH_3Hg_2Cl_5$

in the cases of the ortho and meta compounds and a corresponding aniline salt having been obtained, strenuous efforts were made to get a similar para compound by these methods. The excess of mercuric chloride was gradually increased in successive trials until it began to crystallize out with the salt originally obtained, mixed with it. It seemed strange that in each of the other cases a compound containing one molecule of the basic chloride to two of the mercuric chloride could be obtained, while with the para compound it could not be formed. It could not be obtained by these methods, however, although the conditions were varied through wide ranges as to the excess of mercuric chloride, the amount of water used, the amount of acid added, and the degree of heat employed. This fact suggested the idea that there might be a greater possibility in the other direction with the para compound than with the ortho and meta. With this in view experiments were next made using an excess of the basic chloride in gradually increasing amounts and under varying conditions. The results were invariably the same. The salt above described was formed in every case in quantity sufficient to use up the mercuric chloride, and on evaporation the excess of paratoluidine hydrochloride crystallized from the solution. The salt $C_7H_7NH_3HgCl_3$ is therefore the only paratoluidine chloromercurate which it seems possible to make by these methods. The para salt, on account of its insolubility in cold water and the ease with which it can be crystallized, was probably the most satisfactory of the salts obtained. In its formation it was free from any admixture of the salts having different proportions of the chlorides—a fact which gave trouble, sometimes, in working with the other salts.

### MIXED DOUBLE HALIDES.

No complete investigation has been made in this line, but a few words will be given in order to show the nature and tendency of the work.

4 grams of orthotoluidine hydrochloride and 12 grams of mercuric bromide were weighed into a beaker with about 75 cc. of water, and a few drops of hydrochloric acid added.

(Numerous attempts with water only were failures.) Some mercuric bromide crystallized out and was removed. On longer standing a salt crystallized in beautiful, glistening needles. These were uniform and regular in appearance, and were washed and dried.

Estimations of mercury gave:

|  | Calculated for $C_7H_7NH_3HgBr_2Cl$. | Found. I. | II. |
|---|---|---|---|
| Hg | 39.76 | 40.11 | 40.51 |

The existence of mixed halides of this order seems undoubted. The only difficulty is to get them in good condition. The above is given to show the possibility of their formation.

When a chloride and bromide of the above kinds are mixed there are a number of possibilities—any of these salts may be formed: $HgBr_2$, $HgCl_2$, $C_7H_7NH_3HgBrCl_2$, $C_7H_7NH_3HgBr_2Cl$, and several others which might crystallize out. In some of the experiments all these possibilities seem to be realized in the same beaker, judging from the various crystals formed.

Some of the salts when heated in the mother-liquor melt to heavy oils which sink to the bottom of the beaker. These oils crystallize on cooling, but they have not been fully investigated. At present the most that can be said is that there is no doubt in the mind of the author as to the existence of the mixed salts, and the work on them will be continued.

## CHLOROMERCURATES OF ELEMENTS OF THE SECOND GROUP.

The following salts have been described by Von Bonsdorff:[1]

$HgCl_2.MgCl_2 + 6H_2O$.
$3HgCl_2.MgCl_2 + 5H_2O$.
$HgCl_2.ZnCl_2 + 4H_2O$.
$2HgCl_2.CaCl_2 + 6H_2O$.
$5HgCl_2.CaCl_2 + 8H_2O$.
$2HgCl_2.SrCl_2 + 2H_2O$.
$2HgCl_2.BaCl_2 + 2H_2O$.

Analyses are given for all except the zinc and strontium salts. The general method of preparation used by Von

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[1] Ann. Phys. (Pogg.), **17**, 115.

Bonsdorff was to add mercuric chloride, as long as it would dissolve in the cold, to a saturated solution of the other chloride in water. Then by slow evaporation he would obtain two salts from the same solution, the second crystallizing after the first had been removed. His analyses were performed in a tube or bulb prepared for the purpose. The method in general was this: A weighed quantity of the salt to be analyzed was placed in this weighed bulb, and heated to drive off the water of crystallization which was collected in a calcium-chloride tube and weighed, or allowed to escape, and estimated by the difference in weight of the bulb. Higher heat was now employed, and the mercuric chloride driven off, and estimated either by difference or by having it sublime in another part of the apparatus. The residue gave the basic chloride. Considering the method, his results agree very well indeed with the calculated. The chief difficulty in the prosecution of this work was, as has been the case with much of the work on the double halides, to get pure salts. The salts are so very soluble that when they do crystallize it is difficult to know whether you have a uniform salt or not. In this investigation more work was done upon the magnesium salt than upon any other. The methods of preparation were, in general, used by Von Bonsdorff with some variations. The methods of analysis for mercury and chlorine were those given in the earlier part of this paper. Magnesium was precipitated as pyrophosphate, strontium as carbonate, and barium as sulphate.

*Magnesium Salt.*—Following Von Bonsdorff's directions, mercuric chloride was added to a saturated solution of magnesium chloride. This was heated and filtered. On allowing to stand, or on evaporating slowly, a set of crystals were deposited just as Von Bonsdorff describes them. It is almost impossible to free this salt completely from the mother-liquor. The method pursued was to place it first on the filter-pump, and then quickly remove it and press it between thick folds of drying-paper by means of a press.

The formation of the salt was tried a great many times and a great many products were analyzed. In order to learn whether the water of crystallization could be driven off by heat or not, about a gram of the salt was carefully weighed and put into an air-bath. Heated for eighteen hours at not over 105°, it lost 20.79 per cent. in weight. Continuing the drying for fifteen hours more with the temperature at no time above 102°, the salt lost 46 per cent.

Another specimen lost 20 per cent. while at a temperature of not over 100°. A third specimen lost 12.6 per cent. when dried at a temperature of not over 90°.

Mercuric chloride itself lost about 20 per cent. dried at 90° or below in fifteen hours, and over 65 per cent. when at the same temperature for two or three days.

From these experiments it will be seen that it is impossible to determine the water of crystallization by heating. As the salt does not lose its water of crystallization over sulphuric acid, it could not be determined in this way. The average of a number of analyses of the better specimens obtained gave the following results :

| | Calculated for $MgHg_3Cl_8 + 5H_2O$. | Calculated for $MgHg_3Cl_8 + 6H_2O$. | Found. |
|---|---|---|---|
| Hg | 60.18 | 59.11 | 59.22 |
| Mg | 2.40 | 2.36 | 2.58 |
| Cl | 28.41 | 27.90 | 27.02 |

Von Bonsdorff's analyses calculated with the same atomic weights give :

| | | | | | | |
|---|---|---|---|---|---|---|
| I. | Hg | 60.08 | Mg | 2.46 | Cl | 28.52 |
| II. | Hg | 59.68 | Mg | 2.43 | Cl | 28.28 |

From these figures he deduces the formula with five molecules of water. The formula with six molecules, as is seen, agrees better with the results obtained at this time, but the results are not sufficiently accurate to say with certainty that it has six molecules of water. Von Bonsdorff describes a salt obtained by evaporation of the mother-liquor from this salt. No such salt was obtained, although many and varied attempts were made to obtain it. Solutions were evaporated slowly for days, others more slowly for weeks, and others still more slowly for months, and no such salt was formed. After the first salt ceased to separate in good form all other crystallizations were mixtures of such a nature as to preclude separation. They were, as nearly as could be learned, mixtures of the first salt and one of the chlorides added in the first place. Attempts were also made to form other salts by using varying proportions of the other two chlorides, and by varying the amount of acidification and of dilution, etc.—all with no success.

Some investigations were begun on the chlorides of the other elements of the group. On account of the unfinished condition of the work, only the compounds of strontium and barium will be mentioned.

*Strontium Salt.*—The chlorides of strontium and mercury were brought together as in making the magnesium salt. A crystallized salt was obtained which is very soluble. It crystallizes in transparent plates, but sometimes in very delicate needles or hairs which project from the top of the solution. This latter was the case when a solution at the point of saturation stood in the air. In the morning there would be a crop of these hairs which would dissolve by the heating of the room during the day and re-form again in the night.

Four analyses of good specimens of this salt gave :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Hg | I. | 50.48 | II. | 50.59 | III. | 50.49 | IV. | 50.35 |
| Sr | I. | 8.90 | II. | 8.94 | III. | 9.22 | IV. | 9.13 |

The salt loses water over calcium chloride or sulphuric acid. Several weighed specimens left for some days over sulphuric acid lost from 13.30 per cent. in the case of the smallest amount, to 14.16 per cent. in the case of the largest. Von Bonsdorff gives $SrCl_2.2HgCl_2 + 2H_2O$ as the composition of this salt, but the conclusion arrived at in this work was that it is a compound of the same order as the magnesium salt; *viz.*, $SrHg_3Cl_8 + (H_2O)x$.

No other salt was obtained, although a number of attempts were made to form one.

*Barium Salt.*—A barium salt was formed in the same manner. This, like the strontium salt, lost water even on standing in the air, so that it had to be analyzed immediately after its formation. Two specimens were analyzed after recrystallization with these results :

| | Calculated for $BaHg_2Cl_6 + 8H_2O$. | Found. I. | II. |
|---|---|---|---|
| Hg | 51.54 | 51.87 | 51.63 |
| Ba | 11.77 | 11.84 | 11.89 |

This barium trichloromercurate is less soluble than the other salts, and can, therefore, be prepared more easily and surely.

All the double halides described in this article obey Remsen's law,[1] and all attempts to prepare salts not obeying the law, failed.

# THE DOUBLE HALIDES OF TIN WITH ANILINE AND THE TOLUIDINES.

BY ROBERT L. SLAGLE.[2]

## *Introduction.*

The object of this work was to prepare and study the double chlorides formed by the chlorides of tin with the chlorides of aniline and the toluidines. There are two records in the literature of work done on these compounds, Hofmann[3] says, "Erwähnen will ich noch eines sehr schönen Doppelsalzes, welches chlorwasserstaffsaures Chloranilin mit Zinnchlorür bildet. Beim Vermischen beider Auflösungen bleibt die Flüssigkeit klar, nach einiger Zeit aber erstarrt sie zu einer silberglänzenden Krystalmasse." Hjortdahl[4], prepared and made a crystallographic study of the salts, $(C_6H_5NH_2)_2H_2SnCl_6$ and $(p\text{-}C_7H_7NH_2)_2H_2SnCl_6$, but says nothing of the method of preparing them or of their chemical properties.

The number of recorded double halides of inorganic with organic halides is comparatively small. All of them fall under Remsen's law except the salt $CuCl_2.5C_7H_9N.HCl$, which was described by E. Pomey.[5] No efforts have as yet been made to prepare this salt in this laboratory, but it will receive attention in the course of time.

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[1] This JOURNAL, **11**, 296.

[2] From the Author's Dissertation submitted to the Board of University Studies of the Johns Hopkins University, for the degree of Doctor of Philosophy, June, 1894. The work was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

[3] Ann. Chem. (Liebig). **53**, 27, (1845). [4] Ztschr. Kryst., **6**, 484, 490, (1882).

[5] Compt. rend., **104**, 365, (1887).

In the table below the formulas of the salts described in this paper are given:

*Aniline Salts.*

$C_6H_5NH_3SnCl_3 + H_2O$.
$(C_6H_5NH_3)_2SnCl_4$.
$(C_6H_5NH_3)_2SnCl_6$.
$(C_6H_5NH_3)_2SnCl_6 + 3H_2O$.

*Metatoluidine Salts.*

$C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.
$(C_7H_7NH_3)_2SnCl_6 + H_2O$.

*Orthotoluidine Salts.*

$C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.
$(C_7H_7NH_3)_3SnCl_7 + 2H_2O$.

*Paratoluidine Salts.*

$C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.
$(C_7H_7NH_3)_2SnCl_4$.
$(C_7H_7NH_3)_2SnCl_6 + H_2O$.

*Methods of Analysis.*—The salts were purified for analysis by recrystallization from water acidulated with hydrochloric acid. Determinations of tin and chlorine only were made. After the salt was weighed it was dissolved in water acidulated with a few drops of sulphuric acid. Hydrogen sulphide was passed through slowly for about three hours, and in each case the precipitate stood in the solution over night. The stannous or stannic sulphide was collected on a washed filter, dried and ignited in a weighed porcelain crucible. A small amount of concentrated nitric acid was then added and evaporated slowly. The oxidation was completed by igniting over the blast-lamp. A few small pieces of ammonium carbonate were added to remove any traces of sulphuric acid that might be present. After another ignition the crucible was allowed to cool in a desiccator. The tin was weighed as stannic oxide.

As chlorine cannot be determined in the presence of tin, the tin was removed as sulphide. The problem now was to remove the excess of hydrogen sulphide that remained in the solution. At first this was done by adding cadmium sulphate and precipitating the hydrogen sulphide as cadmium sulphide. This gave satisfactory results, but the following more convenient method was adopted. A stream of carbon dioxide was passed through the solution about two or three hours. This was afterwards heated and allowed to boil for a short time. Silver nitrate was now added. After standing for a time the precipitate was collected in a weighed Gooch crucible, dried in the air-bath at 160°, and weighed.

*Preliminary Experiments.*—In order to decide upon the best solvent for the preparation of the double chlorides, preliminary experiments were tried with water, methyl alcohol and ethyl alcohol, each being acidulated with hydrochloric acid. The chlorides of tin and the aniline and toluidine hydrochlorides were each dissolved separately, heated, and mixed when near the boiling-point. The mixture was then allowed to boil for a minute or two and placed aside to cool. In each case a salt was formed. Although the salts crystallized from the alcohols, they were so extremely soluble, that in the preparation of all the compounds described in this paper, water alone, acidulated with hydrochloric acid, was used as the solvent. As to the manner of working, many points were obtained from the experience of Swan.[1]

## ANILINE SALTS.

*Aniline Chlorostannite*, $C_6H_5NH_3SnCl_3 + H_2O$.—For the preparation of this compound molecular quantities of aniline hydrochloride and stannous chloride were separately dissolved in water acidulated with hydrochloric acid. Each solution was heated very nearly to the boiling-point ; then they were mixed and allowed to boil for a short time. The beaker was set aside to cool. The solution remained clear until the next day, when it was slightly disturbed, and in a moment changed into a mass of beautiful silver-white crystals. As it was impossible to distinguish individual crystals, this mass was redissolved, diluted, and again set aside. The day following, the beaker contained a number of transparent, colorless crystals, spear-like in form, and grouped about several centers. They were removed from the mother-liquor, dried, and recrystallized.

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[1] See preceding article.

Similar experiments were tried, in the one case with aniline hydrochloride, slightly in excess of molecular proportions, and, in the other case, with slight excess of stannous chloride. Crystals were obtained similar to those first described, with this exception that those crystallizing from the solution in which the aniline hydrochloride was in excess are somewhat more opaque than the others. The analyses revealed no difference in composition.

After the salts were recrystallized they were filtered with the aid of the pump, and afterwards set aside between folds of drying-paper. They were then analyzed for tin and chlorine with the following results:

I. 0.3824 gram salt gave 0.1718 gram $SnO_2$.
II. 0.3161 gram salt gave 0.1410 gram $SnO_2$.
III. 0.3161 gram salt gave 0.4011 gram AgCl.
IV. 0.2567 gram salt gave 0.3263 gram AgCl.

| | Calculated for | Found. | | | |
|---|---|---|---|---|---|
| | $C_6H_5NH_3SnCl_3 + H_2O$. | I. | II. | III. | IV. |
| Sn | 35.28 | 35.15 | 35.16 | .... | .... |
| Cl | 31.51 | .... | .... | 31.38 | 31.43 |

*Properties.*—Aniline chlorostannite dissolves slowly in cold water, but very readily in hot water. In a short time these solutions become turbid, probably in consequence of the formation of a basic chloride of tin. It is easily soluble in dilute hydrochloric acid, nitric acid, and sulphuric acid, also in concentrated hydrochloric acid, and nitric acid, but very slightly soluble in cold, concentrated sulphuric acid. The nitric-acid solutions turn yellow when heated, and give off the odor of phenol or a nitro-phenol. The salt is extremely soluble in methyl and ethyl alcohols, coloring the latter yellow, but almost insoluble in ether.

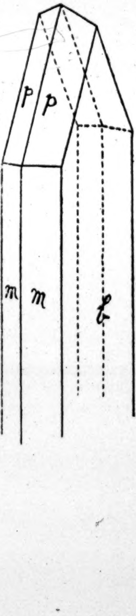
When heated, the salt begins to decompose at about 70°, as is shown by the condensation of white fumes upon the sides of the tube in which it is heated. At about 110° the salt melts and changes to a yellow color. Some of the salt was heated to a higher temperature; a white crystalline product was deposited on the sides of the tube. This was collected and analyzed for chlorine.

0.0678 gram gave 0.0756 gram AgCl, which corresponds to 27.59 per cent. Cl. Calculated Cl for $C_6H_5NH_3Cl$ is 27.39 per cent. From this we conclude that when heated the salt breaks down into stannous chloride and aniline hydrochloride.

One of the beakers containing crystals of the aniline chlorostannite in the hydrochloric-acid mother-liquor was allowed to stand for a time in a desiccator. The crystals gradually went into solution. After four weeks new crystals which had formed in tufts were taken out, dried, and analyzed. When hydrogen sulphide was passed through the solution, yellow stannic sulphide was precipitated. The crystals were not pure, and hence did not give sharp results.

I. 0.2227 gram salt gave 0.0623 gram $SnO_2$.
II. 0.1228 gram salt gave 0.2033 gram AgCl.

| | Calculated for $(C_6H_5NH_3)_2SnCl_6$. | Found. I. | II. |
|---|---|---|---|
| Sn | 22.89 | 22.00 | .... |
| Cl | 40.91 | .... | 40.94 |



These results show that in hydrochloric-acid solution $C_6H_5NH_3SnCl_3 + H_2O$ passes over into $(C_6H_5NH_3)_2SnCl_6$, from the stannous to the stannic condition.

*Crystallography of the Salt.*[1]—The crystals of aniline chlorostannite are tabular in habit, parallel to the brachypinacoid, with a pyramidal termination at one end only. When fresh the crystals are transparent and colorless, but on exposure become opaque. The crystal planes are more or less imperfect, and give indistinct signals, when examined on the reflection-goniometer. The orthorhombic character of a number of these crystals was determined by measurements, the best of which are tabulated below. The crystals measured were about 3 by 10 mm.

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[1] By Mr. Geo. Otis Smith.

Orthorhombic : $\breve{a}:\bar{b}:c = 0.4164:1:0.4608$.

Forms observed:

$p = (111)$ P ; $b = (010)\ \infty$ P $\breve{\infty}$ $m = (110) \infty$ P.

| Angles. | Observed. | Calculated. |
|---|---|---|
| $b:m = (010):(110)$ | *112° 33′ 30″ | ... |
| $m:p = (110):(111)$ | *130° 34′ 15″ | ... |
| $m:p = (110):(\bar{1}11)$ | 130° 40′ | 130° 34′ 15″ |
| $m:m = (110):(1\bar{1}0)$ | 134° 52′ 30″ | 134° 53′ |

The orthorhombic character was verified by an optical examination, which showed the extinction on 010 to be parallel, and the plane of the optic axes, parallel to 001, with the acute bisectrix normal to 010.

*Di-aniline Chlorostannite*, $(C_6H_5NH_3)_2SnCl_4$.—After the preparation of the aniline chlorostannite, one molecule of stannous chloride was added to two molecules of aniline chlorostannite first separated from the solution. These were removed, and the mother-liquor concentrated. Crystals of an entirely different appearance now separated. These were removed, dried in the air, and analyzed for tin and chlorine with the following results:

I. 0.2529 gram salt gave 0.0836 gram $SnO_2$.
II. 0.2753 gram salt gave 0.0914 gram $SnO_2$.
III. 0.2529 gram salt gave 0.3182 gram AgCl.
IV. 0.2753 gram salt gave 0.3484 gram AgCl.

| | Calculated for $(C_6H_5NH_3)_2SnCl_4$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Sn | 26.52 | 26.05 | 26.16 | .... | .... |
| Cl | 31.58 | .... | .... | 31.11 | 31.29 |

The observed properties of this salt are similar to those of the aniline chlorostannite, except that it is very much more soluble. The crystals are transparent when fresh, and very well defined, but the uneven surfaces did not admit of accurate measurement. They belong to the monoclinic system.

Attempts were made to prepare other compounds of stannous chloride and aniline hydrochloride, the two salts having been mixed in all proportions, from four molecules of stannous chloride and one molecule of aniline hydrochloride to one molecule of stannous chloride and four of aniline hydrochloride. No other salts were obtained. When the stannous chloride was in excess, aniline chlorostannite was formed. When the aniline hydrochloride was in excess, di-aniline chlorostannite separated from the solution. When these were removed and the mother-liquors concentrated, either stannous chloride or aniline hydrochloride would separate.

*Di-aniline Chlorostannate*, $(C_6H_5NH_3)_2SnCl_6 + 3H_2O$.—When molecular quantities of stannic chloride and aniline hydrochloride were dissolved in dilute hydrochloric acid, mixed and boiled, crystals began to form before the liquid cooled down to the temperature of the room. They were very well defined, uniform and in sheaf-like clusters. After standing in the mother-liquor over night, they were removed and dried. In twenty-four hours they became opaque, losing all their water of crystallization. In order to get these crystals again, fresh quantities of stannic chloride and aniline hydrochloride were used. The same sheaf-like clusters were observed. These were removed from the mother-liquor, dried between layers of drying-paper, and at once analyzed. As it was impossible to dry the crystals thoroughly without loss of water of crystallization, the analyses were not very sharp. The following are the best results obtained :

I. 0.1330 gram salt gave 0.0342 gram $SnO_2$.
II. 0.3489 gram salt gave 0.0898 gram $SnO_2$.
III. 0.1330 gram salt gave 0.1994 gram AgCl.
IV. 0.1296 gram salt gave 0.1954 gram AgCl.

| | Calculated for $(C_6H_5NH_3)_2SnCl_6 + 3H_2O$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Sn | 20.74 | 20.26 | 20.30 | .... | .... |
| Cl | 37.06 | .... | .... | 37.08 | 37.20 |

Attempts were now made to get the anhydrous crystals mentioned above in a pure form for study. Repeated recrystallizations produced two different kinds of crystals, one kind arranged very closely in tufts, the other comparatively long and straight. It was impossible to obtain a uniform set. They were at last separated mechanically and analyzed, and found to be of identical composition.

I. 0.2008 gram salt gave 0.0588 gram $SnO_2$.
II. 0.2904 gram salt gave 0.0850 gram $SnO_2$.
III. 0.2666 gram salt gave 0.4410 gram AgCl.
IV. 0.1802 gram salt gave 0.2980 gram AgCl.

| | Calculated for $(C_6H_5NH_3)_2SnCl_6$. | Found.<br>I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Sn | 22.89 | 23.08 | 23.07 | .... | .... |
| Cl | 40.91 | .... | .... | 40.90 | 40.90 |

*Properties.*—It dissolves in water. After standing a longer time than in the case of the stannous compounds the solution becomes turbid. The same turbid appearance occurs when it is dissolved in dilute sulphuric acid. In other respects it closely resembles the stannous compounds. The crystals of this salt are transparent, and change very slowly when in contact with the air. A crystallographic study of these compounds has been made by Hjortdahl.[1]

All attempts to make other compounds of stannic chloride and aniline hydrochloride, by having the one or the other salt in excess, failed.

## ORTHOTOLUIDINE SALTS.

*Orthotoluidine Chlorostannite*, $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.—In studying the compounds formed with the three toluidines, the line of work was similar to that in the case of aniline. Stannous chloride and orthotoluidine hydrochloride were mixed in all proportions, from two molecules stannous chloride and one molecule orthotoluidine hydrochloride to one molecule of stannous chloride and four of orthotoluidine hydrochloride. In each beaker beautiful white opaque crystals separated from the solution. These were taken from the mother-liquor, dried in the air, and analyzed. The mother-liquors were concentrated and crystals were again formed and removed. Only one double salt was obtained. At the one extreme, stannous chloride separated from the solution, and at the other extreme orthotoluidine hydrochloride separated.

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[1] *Loc. cit.*

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The crystals were analyzed for tin and chlorine with the following results:

I. 0.5107 gram salt gave 0.2267 gram $SnO_2$.
II. 0.4933 gram salt gave 0.2187 gram $SnO_2$.
III. 0.1792 gram salt gave 0.2248 gram AgCl.
IV. 0.3837 gram salt gave 0.4813 gram AgCl.

| | Calculated for $C_7H_7NH_3SnCl_5 + \frac{1}{2}H_2O$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Sn | 34.87 | 34.98 | 34.94 | .... | .... |
| Cl | 31.04 | .... | .... | 31.02 | 31.02 |

Doubt as to the presence of the half-molecule of water having arisen, the salt was slowly dried at a temperature of about 70°. Owing to the ready decomposition and the volatility of these compounds, not much reliance was placed on this as a general method for the determination of the water. In this case two specimens of the salt were weighed, and heated for about twenty-four hours at 70°. After this a qualitative examination showed that no more water was present.

0.3843 gram salt lost in weight 0.0106 gram, corresponding to 2.75 per cent. $H_2O$.

0.4345 gram salt lost in weight 0.0117 gram, corresponding to 2.69 per cent. $H_2O$.

Calculated $H_2O$ for $C_7H_7NH_3SnCl_5 + \frac{1}{2}H_2O$ is 2.62 per cent.

This salt crystallizes in prisms, but no crystals perfect enough for measurement were obtained.

*Tri-orthotoluidine Chlorostannate*, $(C_7H_7NH_2)_3SnCl_7 + 2H_2O$. —Stannic chloride and orthotoluidine hydrochloride were mixed in molecular proportions and treated in the usual manner. Soon after the solution began to cool, crystals appeared. The simple chlorides were also mixed in all proportions, from two molecules of stannic chloride and one molecule of orthotoluidine hydrochloride to one molecule of stannic chloride and six molecules of orthotoluidine hydrochloride. Crystals appeared in each beaker; these were removed and purified by recrystallization. Although the mother-liquors were concentrated and new crops of crystals removed, the analyses showed that only one double salt of stannic chloride and orthotoluidine hydrochloride was formed.

I. 0.3372 gram salt gave 0.0694 gram $SnO_2$.
II. 0.1378 gram salt gave 0.0286 gram $SnO_2$.
III. 0.3205 gram salt gave 0.4424 gram AgCl.
IV. 0.3372 gram salt gave 0.4649 gram AgCl.

| | Calculated for $(C_7H_7NH_3)_3SnCl_7 + 2H_2O$. | Found.<br>I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Sn | 16.37 | 16.22 | 16.36 | .... | .... |
| Cl | 34.10 | .... | .... | 34.13 | 34.09 |

### METATOLUIDINE SALTS.

*Metatoluidine Stannite*, $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.—As in the case of the orthotoluidine compounds, stannous chloride and metatoluidine hydrochloride were mixed in different proportions, from a large excess of stannous chloride to a large excess of metatoluidine hydrochloride. In each case beautiful silver-white, opaque crystals separated in very thin leaflets. Analyses showed that these are identical. The results of the determinations of tin and chlorine are as follows:

I. 0.2516 gram salt gave 0.1119 gram $SnO_2$.
II. 0.2848 gram salt gave 0.1258 gram $SnO_2$.
III. 0.2848 gram salt gave 0.3581 gram AgCl.
IV. 0.2147 gram salt gave 0.2706 gram AgCl.

| | Calculated for $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$. | Found.<br>I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Sn | 34.79 | 35.05 | 34.81 | .... | .... |
| Cl | 31.05 | .... | .... | 31.09 | 31.12 |

The general properties of this salt are similar to those of the corresponding aniline compound. It changes over into the stannic condition when allowed to stand in hydrochloric-acid solution for a few weeks, the solution changing to a dark color. Owing to lack of time a quantitative study of this reaction was not made.

*Di-metatoluidine Chlorostannate*, $(C_7H_7NH_3)_2SnCl_6 + H_2O$.—This salt has a very strong crystallizing force, and is easily obtained by mixing stannic chloride and metatoluidine hydrochloride in any proportion. If the toluidine hydrochloride is in great excess, the crystals that separate from the solution will be mixtures of it and the di-toluidine chlorostannate. These crystals were purified by recrystallization, removed from the mother-liquor, and dried in the air. Analyses for tin and chlorine gave the following results :

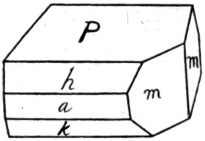
I. 0.2434 gram salt gave 0.0650 gram $SnO_2$.
II. 0.2693 gram salt gave 0.0721 gram $SnO_2$.
III. 0.2434 gram salt gave 0.3689 gram AgCl.
IV. 0.2693 gram salt gave 0.4091 gram AgCl.

| | Calculated for $(C_7H_7NH_3)_2SnCl_6 + H_2O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Sn | 21.04 | 21.06 | 21.10 | .... | .... |
| Cl | 37.59 | .... | .... | 37.48 | 37.56 |

*Crystallography of the Salt.*[1]—The crystals of di-metatoluidine chlorostannate are tabular, parallel to the basal pinacoid. They are transparent and only faintly tinged with red, often showing an hour-glass arrangement with different shades of color.

Only one of the crystals gave distinct signals, when examined on the reflecting-goniometer, although good crystal-faces were developed on most of the crystals. The measurements showed the crystal to be monoclinic, and this result was verified by an optical examination.

Five forms were determined on this crystal, and another crystal showed the clino-pinacoid also to be present, although measurements could not be made. Cleavages parallel to the basal pinacoid and clino-pinacoid were observed.



The forms determined, the angles observed and calculated, and the axial constants determined are tabulated below :

$$\text{Monoclinic}: \breve{a} : \bar{b} : \acute{c} = 1.924 : 1 : 1.463$$
$$\beta = 86° \, 3'$$

Forms: $P = \{001\}\, 0P$
$h = \{101\}\, -\bar{P}\infty$
$k = \{10\bar{1}\}\, +\bar{P}\infty$
$a = \{100\}\, \infty\bar{P}\infty$
$m = \{120\}\, \infty\grave{P}2$

---

[1] By Mr. Geo. Otis Smith.

| Angles. | Observed. | Calculated. |
|---|---|---|
| $P:a=(001):(\bar{1}00)$ | *86° 38′ | ... |
| $P:a=(001):(100)$ | 93° 6′ | 93° 22′ |
| $m:m=(120):(\bar{1}20)$ | *38° 34′ | ... |
| $m:m=(\bar{1}20):(1\bar{2}0)$ | 38° 34′ | 38° 34′ |
| $P:h=(001):(101)$ | 143° 54′ | 144° 3′ |
| $P:k=(001):(\bar{1}01)$ | *141° 36′ | ... |

## PARATOLUIDINE SALTS.

*Paratoluidine Chlorostannite*, $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$.—Stannous chloride and paratoluidine hydrochloride were mixed in all proportions, from three molecules of stannous chloride and one molecule of paratoluidine hydrochloride to one molecule of stannous chloride and four of paratoluidine hydrochloride. In each beaker crystals were very easily obtained. These all appeared to be identical, but analyses showed that the simple chlorides unite in two different proportions. When the simple chlorides were mixed in molecular proportions, and when the stannous chloride was in excess, paratoluidine chlorostannite was formed. The crystals were removed and dried in the usual manner. Analyses for tin and chlorine gave the following results :

I. 0.2421 gram salt gave 0.1071 gram $SnO_2$.
II. 0.1901 gram salt gave 0.0839 gram $SnO_2$.
III. 0.2814 gram salt gave 0.3498 gram AgCl.
IV. 0.2596 gram salt gave 0.3235 gram AgCl.

|  | Calculated for $C_7H_7NH_3SnCl_3 + \frac{1}{2}H_2O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Sn | 34.79 | 34.86 | 34.78 | .... | .... |
| Cl | 31.05 | .... | .... | 30.74 | 30.81 |

This salt is very well defined crystallographically. The crystals were of a light-yellow color, not perfect enough for measurement.

The properties of this salt are, in general, similar to those of the corresponding aniline salt. After standing a few weeks in dilute hydrochloric-acid solution, it changes color and passes over into the stannic condition.

*Di-paratoluidine Chlorostannite*, $(C_7H_7NH_3)_2SnCl_4$.—When one molecule of stannous chloride was added to two molecules of paratoluidine hydrochloride, and when the latter was in excess of this proportion, crystals were formed which resembled the paratoluidine chlorostannite. These were analyzed with the following results:

I. 0.2522 gram salt gave 0.0784 gram $SnO_2$.
II. 0.2692 gram salt gave 0.3239 gram AgCl.
III. 0.3026 gram salt gave 0.3659 gram AgCl.

| | Calculated for $(C_7H_7NH_3)_2SnCl_4$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Sn | 24.96 | 24.50 | .... | .... |
| Cl | 29.72 | .... | 29.75 | 29.90 |

This salt is much more soluble than the paratoluidine chlorostannite. The mother-liquors were concentrated and new crops of crystals were obtained. Analysis showed that these were either one of the double salts above described or paratoluidine hydrochloride. We therefore concluded that stannous chloride and paratoluidine hydrochloride form only two double salts.

*Di-paratoluidine Chlorostannate*, $(C_7H_7NH_3)_2SnCl_6 + H_2O$. —The stannic chloride and paratoluidine hydrochloride were mixed in all proportions, from two molecules of stannic chloride and one molecule of paratoluidine hydrochloride to one molecule of stannic chloride and four of paratoluidine hydrochloride. The compound formed had a stronger crystallizing force than any other salt of this series. Analyses showed that only one double salt was formed by these two chlorides.

I. 0.4970 gram salt gave 0.1309 gram $SnO_2$.
II. 0.5205 gram salt gave 0.1385 gram $SnO_2$.
III. 0.5205 gram salt gave 0.7929 gram AgCl.
IV. 0.3478 gram salt gave 0.5292 gram AgCl.

| | Calculated for $(C_7H_7NH_3)_2SnCl_6 + H_2O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Sn | 21.04 | 20.76 | 20.97 | .... | .... |
| Cl | 37.59 | .... | .... | 37.65 | 37.61 |

A crystallographic study of this salt has been made by Hjortdahl.[1] The crystals are transparent, of a light-yellow color. They effloresce slowly when in contact with the air.

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[1] *Loc. cit.*

All efforts made to obtain other salts of stannic chloride and paratoluidine hydrochloride met with failure.

Whether other double salts of the chlorides of tin with the chlorides of aniline and the toluidines exist or not it is impossible to say, but it can be said that careful attempts, which were unsuccessful, were made to prepare other salts by the method already described. The properties and solubilities of these compounds were not as thoroughly studied as desired on account of lack of time. Another interesting fact that was not thoroughly investigated is the change of the stannous salts to the stannic condition when allowed to stand several weeks in dilute hydrochloric-acid solution. In the case of aniline, however, it was shown that the aniline chlorostannite changed into di-aniline chlorostannate. After standing four months, the color of the solution had changed through red to almost black, a change similar to that which aniline alone undergoes.

# ON DOUBLE HALIDES OF ZINC WITH ANILINE AND THE TOLUIDINES.

BY DANIEL BASE.[1]

In the continuation of the investigation of double halides containing organic bases, it seemed desirable to study those of zinc with aniline and the toluidines, an account of which is given in this paper. As the halides of the organic bases are closely related to the ammonium halides, and as a number of zinc ammonium double chlorides are recorded in the literature, some of which do not conform to the law and the authority for which might be questioned, it seemed proper, at the same time, to make a study of these compounds. This work will be spoken of in the latter part of this paper.

All the double salts of zinc with inorganic as well as organic halides, that have been recorded in the journals up to the present, have been collected and tabulated. For the sake of completeness, it is thought well to give a list of these salts with the references.

---

[1] From the Author's Dissertation submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1895. The work was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

### *Double Chlorides.*

$ZnCl_2.2NH_4Cl.H_2O$. Geiger's and Liebig's Mag., **36**, 43 : Schindler.

$ZnCl_2.2NH_4Cl.H_2O$. Ann. Chem. (Liebig), **66**, 280 : Hautz.

$ZnCl_2.NH_4Cl.2H_2O$. *Ibid*, **66**, 280 : Hautz.

$ZnCl_2.2NH_4Cl$. Ann. der Phys. Pogg., **94**, 507 : Rammelsberg.

$ZnCl_2.NH_4Cl$. Ann. des Mines (5), **12**, 1 : Marignac.

$ZnCl_2.3NH_4Cl$. Ann. des Mines (5), **12**, 1 : Marignac.

$ZnCl_2.3NH_4Cl.H_2O$. Ann. chim. phys. [6], **11**, 308 : Berthelot and André.

$ZnCl_2.6NH_4Cl.\frac{2}{3}H_2O$. *Loc. cit.* : Berthelot and André.

$ZnCl_2.4NH_4Cl$. Bull. Soc. Chim. (1861), 51 : Dehérain.

$ZnCl_2.2KCl$. Ann. der Phys. Pogg., **94**, 507 : Rammelsberg.

$ZnCl_2.2HCl$. Ann. des Mines [5], **12**, 1 : Marignac.

$ZnCl_2.2NaCl.3H_2O$. *Ibid* [5], **12**, 1 : Marignac.

$ZnCl_2.BaCl_2.4H_2O$. Chem. News, **27**, 271 ; and **28**, 186: G. Warner.

$ZnCl_2.MgCl_2.6H_2O$. *Ibid.*

$ZnCl_2.3CsCl$. Am. J. Sci. [3], **46**, 425 : Wells and Campbell.

$ZnCl_2.2CsCl$. *Loc. cit.* : Wells and Campbell.

$ZnCl_2.PtCl_2.6H_2O$. Jour. prakt. Chem. [2], **15**, 277 : Nilson.

$ZnCl_2.PtCl_4.6H_2O$. Jsb. Chem. (1870), 393 : Topsoë.

$ZnCl_2.PdCl_4.6H_2O$. *Ibid.* (1870), 393 : Topsoë.

$ZnCl_2.2AuCl_3.8H_2O$. Wien. Akad. Ber. (2 Abth.), **69**, 266 : Topsoë.

$ZnCl_2.2AuCl_3.12H_2O$. Ann. der Phys. (Pogg.), **17**, 261; **33**, 64 : Von Bonsdorff.

$ZnCl_2.2AuCl_3$. *Ibid*, **17**, 261 ; **33**, 64 : Von Bonsdorff.

### *Double Chlorides with Organic Constituents.*

$ZnCl_2.2C_9H_{14}N_2.HCl$(Cyanconiïne). J. prakt. Chem. [2], **22**, 281 : E. v. Meyer.

$ZnCl_2.2C_9H_7N.HCl$(Quinoline). Ber. d. chem. Ges., **15**, 645 : Wallach.

$ZnCl_2$.2(Tetraethyldiamidotriphenylcarbinol.2HCl). Ann. Chem. (Liebig), **217**, 223 : Döbner.

$ZnCl_2$.(*p*-Amido-*o*-imidophenylurea). Ber. d. chem. Ges., **17**, 2632 : Hager.

$ZnCl_2$.(Quinine.2HCl).$2H_2O$. *Ibid*, **18**, 1225 : Comstock and Königs.

$ZnCl_2$.2(Papaverin.HCl). Monatshefte, **6**, 667 : Goldschmidt.

$ZnCl_2$.(β-Picolin.HCl). Ber. d. chem. Ges., **18**, 3091 : Ad. Hesekiel.

$ZnCl_2$.2(α-γ-Dimethylquinoline.HCl). Jour. prakt. Chem. [2], **33**, 393. C. Beyer.

$ZnI_2$.2(Papaverin.HCl). Monatshefte, **7**, 506 : Jahoda.

$ZnCl_2$.2(Ethenyltriamidonaphthalene.HCl). J. Chem. Soc., **51**, 607 : Meldola and Streatfield.

$ZnCl_2$.(Isocinchonine.2HCl). Ber. d. chem. Ges., **20**, 2510 : Comstock and Königs.

$ZnCl_2.2C_6H_8N.HCl$. *Ibid*, **21**, 1578 : Lang.

$ZnCl_2$.(Dipyridin.2HCl). J. Chem. Soc. [2], **7**, 411 : Anderson.

*Double Bromides.*

$ZnBr_2.2CsBr$. Am. J. Sci. [3], **46**, 425 : Wells and Campbell.

$ZnBr_2.3CsBr$. *Loc. cit.* : Wells and Campbell.

$ZnBr_2.2NH_4Br$. Jsb. Chem. (1860), 17 : Boedeker.

$3ZnBr_2.2DiBr_3.36H_2O$. Ann. Chem. (Liebig), **191**, 342 : Frerichs and Smith.

$3ZnBr_2.DiBr_3.12H_2O$. Bull. Soc. Chim. [2], **43**, 361 : P. T. Cleve.

$3ZnBr_2.2LaBr_3.39H_2O$. Ann. Chem. (Liebig), **191**, 357 : Frerichs and Smith.

$ZnBr_2.PtBr_4.12H_2O$. N. Archiv. ph. nat., **35**, 58 : Topsoë.

*Double Iodides.*

$ZnI_2.2NH_4I$. Ann. der Phys. (Pogg.), **43**, 665 : Rammelsberg.

$ZnI_2.KI$. *Loc. cit.* : Rammelsberg.

$ZnI_2.2NaI.3H_2O$. *Loc. cit.* : Rammelsberg.

$2ZnI_2BaI_2$. *Loc. cit.*: Rammelsberg.

$ZnI.As(CH_3)_4I$ (old formula). Compt. rend., **49**, 87 : Cahours.

$ZnI.As(C_2H_5)_4I$ (old formula). *Loc. cit.* : Cahours.

$ZnI.P(C_2H_5)_4I$ (old formula). Ann. chim. phys. [3], **62**, 333 : Cahours.

$ZnI.P(C_2H_5)3HI$ (old formula). *Loc. cit.*: Cahours.

$3ZnI_2.2DiI_3.24H_2O$. Ann. Chim. (Liebig), **191**, 343: Frerichs and Smith.

$3ZnI_2.2LaI_3.27H_2O$. *Loc. cit.* : Frerichs and Smith.

$ZnI_2PtI_4.9H_2O$. N. Archiv. ph. nat., **38**, 297 : Topsoë.

$ZnI_2.2CsI$. Am. J. Sci. [3], **46**, 425 : Wells and Walden.

$ZnI_2.3CsI$. *Loc. cit.* : Wells and Walden.

### *Double Fluorides.*

$ZnFl.SiFl_2.6HO$ (old formula). Ann. des Mines [5], **15**, 221 : Marignac.

$ZnFl_2.TaFl_5.7H_2O$. Ann. chim. phys. [4], **19**, 274 : Marignac.

$ZnFl_2.SnFl_4.6H_2O$. Ann. des Mines [5], **15**, 221 : Marignac.

$ZnFl_2.2KFl$. Ann. der Phys. (Pogg.), **1**, 26 : Berzelius.

$ZnFl_2.Al_2Fl_6$. *Loc. cit.* : Berzelius.

$ZnFl_2.KFl$. Ber. d. chem. Ges., **19**, 896 : Wagner.

$ZnFl_2.NaFl$. *Loc. cit.*: Wagner.

$ZnFl_2.2NH_4Fl.2H_2O$. *Loc. cit.*: Wagner.

$ZnFl_2.2BFl_3$. *Loc. cit.*: Wagner.

$2ZnFl_2.Mn_2Fl_6.8H_2O$. J. prakt. Chem. [2], **34**, 41 : Christensen.

All of the salts included in the above list, with one exception, are in harmony with the law of composition of double halides pointed out by Professor Remsen.[1] The exception is the ammonium compound of the formula $ZnCl_2.6NH_4Cl.\frac{2}{3}H_2O$ described by Berthelot and André. It will, however, be shown in this article that this salt cannot be obtained.

*Methods of Analysis*.—The salts were analyzed for zinc, halogen, and water of crystallization when present. Zinc was precipitated as carbonate and weighed as oxide. The organic bases had no solvent action on the zinc carbonate, as ammonia has when present in the solution.

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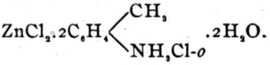
[1] This JOURNAL, **11**, 296.

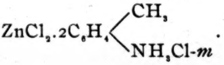
Chlorine was determined gravimetrically or volumetrically by Volhard's method.

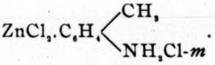
*Compounds Described.*

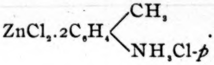
Dianiline chlorozincate, $ZnCl_2.2C_6H_5.NH_3Cl.H_2O$.

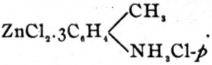
Trianiline chlorozincate, $ZnCl_2.3C_6H_5.NH_3Cl.2H_2O$.

Diorthotoluidine chlorozincate,

$ZnCl_2.2C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Cl\text{-}o\end{matrix}\right..2H_2O.$

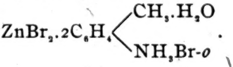
Dimetatoluidine chlorozincate,

$ZnCl_2.2C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Cl\text{-}m\end{matrix}\right..$

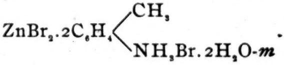
Trimetatoluidine chlorozincate,

$ZnCl_2.C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Cl\text{-}m\end{matrix}\right..$

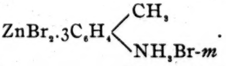
Diparatoluidine chlorozincate,

$ZnCl_2.2C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Cl\text{-}p\end{matrix}\right..$

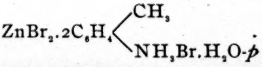
Triparatoluidine chlorozincate,

$ZnCl_2.3C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Cl\text{-}p\end{matrix}\right..$

Dianiline bromozincate, $ZnBr_2.2C_6H_5NH_3BrH_2O$.

Diorthotoluidine bromozincate,

$ZnBr_2.2C_6H_4\left\langle\begin{matrix}CH_3.H_2O\\NH_3Br\text{-}o\end{matrix}\right..$

Dimetatoluidine bromozincate,

$ZnBr_2.2C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Br.\,2H_2O\text{-}m\end{matrix}\right..$

Trimetatoluidine bromozincate,

$ZnBr_2.3C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Br\text{-}m\end{matrix}\right..$

Diparatoluidine bromozincate,

$ZnBr_2.2C_6H_4\left\langle\begin{matrix}CH_3\\NH_3Br.H_2O\text{-}p\end{matrix}\right..$

Diammonium chlorozincate, $ZnCl_2.2NH_4Cl$.

Triammonium chlorozincate, $SnCl_2.3NH_4Cl$.

*Double Chlorides.*

*Dianiline Chlorozincate*, $ZnCl_2.2C_6H_5NH_3Cl.H_2O$. — This salt was made by H. Vohl[1], in 1865, in an indirect way. In an article, "On the Compounds of Zinc Chloride with Aniline and the Application of the Same in the Arts," Vohl describes the preparation of the salt $ZnCl_2.2C_6H_5NH_2$. According to him it forms shining white needles, which can be crystallized from alcohol, but are decomposed by water. In dilute hydrochloric acid the compound is easily soluble and yields a salt crystallizing in large colorless columnar crystals and plates, which become colored violet-blue in contact with the air. This salt is easily soluble in alcohol and water. It contains water of crystallization, which escapes completely at 105° C. Heated more strongly it melts, vapors of aniline hydrochloride are formed, while zinc chloride remains behind, which takes on a violet-blue color.

This description of the double salt by Vohl was found to be correct, and his analyses were good, showing the salt to have the above formula. His object in making the double salts was to prepare aniline dyes in accordance with the method in use at that time. By mixing the double salt with an oxidizing agent, as mercurous nitrate, and heating, magenta was formed. Vohl made no systematic study of double salts nor had he any idea of getting more than one aniline salt, and therefore a repetition of the work in a thorough manner was necessary, especially as the object now is to get evidence for or against the law of composition of double salts. My work has shown that there are two double aniline salts, one being identical with that described by Vohl.

When zinc chloride and aniline hydrochloride are mixed so that the number of molecules of the former to that of the latter bear these relations, 3 : 1, 2 : 1, 1 : 1, 1 : 2, dianiline chlorozincate is formed in every case. It seems to make no difference whether the solutions are heated or not, or whether they are neutral or made acid. The solutions soon change color to a reddish-brown, or greenish color, even when mixed in the cold. The ease with which they become colored varies with the proportion of aniline hydrochloride present. Alcoholic solutions color extremely rapidly. On standing, a flocculent greenish material is formed in the solutions. The shape of the crystals varies with conditions. The most frequent form is the plates spoken of by Vohl, which belong to the triclinic system. The salt is easily purified by recrystallization from water. When pure it does not change color readily in the air. It loses all its water in the sulphuric-acid desiccator, the weight remaining constant after transferring to an air-bath and heating to 100° C. It is extremely soluble in methyl alcohol, so much so that it cannot be recrystallized from this. It is less soluble in ethyl alcohol.

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[1] Ding. poly. J., **175**, 211.

0.459 gram salt gave 0.0904 gram ZnO and 0.6365 gram AgCl.

0.3912 gram salt gave 0.0772 gram ZnO and 0.5408 gram AgCl.

0.4405 gram salt lost 0.0191 gram water.

| | Calculated for $ZnCl_2.2C_6H_5NH_2Cl.H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Zn | 15.77 | 15.81 | 15.82 | .... |
| Cl | 34.32 | 34.3 | 34.18 | .... |
| $H_2O$ | 4.35 | .... | .... | 4.34 |

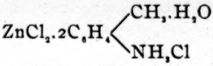
*Trianiline Chlorozincate*, $ZnCl_2.3C_6H_5NH_3Cl.2H_2O$.—When zinc chloride and aniline hydrochloride are brought together in water solution so that the molecular proportions of the former to the latter are as 1 : 3, 1 : 4, 1 : 6, trianiline chlorozincate is formed. The 1 : 3 mixture yields the dianiline salt also, which can easily be separated from the trianiline salt on account of its totally different form. The solutions soon become deeply colored, but the crystals are colored only a little, and by washing with water are pure enough for analysis. When pure they are colorless. The salt is more soluble in water and alcohol than the dianiline salt. It is stable in the air, but on long exposure it turns green. It loses all its water in the sulphuric-acid desiccator, and can be heated in the air-bath to 100° without decomposition. It forms long prisms apparently of the orthorhombic system. The forms are unit prism and macro prism.

0.3538 gram salt gave 0.051 gram ZnO and 0.4536 gram AgCl.

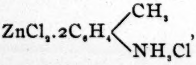
0.2875 gram salt gave 0.042 gram ZnO and 0.369 gram AgCl.

0.2194 gram salt lost 0.0143 gram $H_2O$.

| | Calculated for $ZnCl_2.3C_6H_5NH_3Cl.2H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Zn | 11.62 | 11.57 | 11.74 | .... |
| Cl | 31.58 | 31.7 | 31.75 | .... |
| $H_2O$ | 6.41 | .... | .... | 6.52 |

*Diorthotoluidine Chlorozincate*,  $ZnCl_2.2C_6H_4\left\langle\begin{array}{l}CH_3.H_2O\\NH_3Cl\end{array}\right.$.—This compound was prepared in 1865 by Gräfinghoff,[1] who made a study of the action of the toluidines (ortho and para) on zinc chloride. He was led to this study by the work of Vohl, already referred to. His object was the same as Vohl's, that is, the preparation of compounds of zinc chloride with toluidine for technical application in the preparation of dyes. On treating the toluidine compound with hydrochloric acid, drying on the water-bath, and taking up with alcohol, he says he obtained the salt $ZnCl.2C_7H_9N.HCl$. This salt, he says, can also be prepared directly from zinc chloride and toluidine hydrochloride, and when obtained from water solution contains water of crystallization, but when obtained from alcohol it contains no water. He says further, "to avoid the objection that the existence of these salts was shown only for the liquid toluidine, toluidine was prepared from pure toluene from tolu balsam, which, according to Muspratt and Hofmann, was solid. Salts were formed in the same manner and analyzed, and their identity with those from the liquid toluidine shown. They agreed in solubility and physical properties perfectly with the latter.

Gräfinghoff's object evidently was not to make a systematic study of double halides.

Bibanow[2] also says he obtained from a mixture of orthotoluidine hydrochloride and a concentrated solution of zinc chloride, by cooling down to —5°, a salt of the composition  $ZnCl_2.2C_6H_4\left\langle\begin{array}{l}CH_3\\NH_3Cl\end{array}\right.$, having no water of crystallization and forming colorless concentrically grouped plates.

Zinc chloride and orthotoluidine hydrochloride were brought together in aqueous solution in the molecular proportions 3:1,

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[1] J. prakt. Chem., 95, 221.

[2] Mon. scient. (3), 4, 925.

2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4. In the last case the toluidine hydrochloride separated out first. The solutions were heated to boiling, and it mattered not whether they were made acid or not. They did not change color nearly so rapidly as the solutions containing zinc chloride and aniline chloride, and they deposited very little of the green flocculent material.

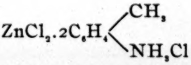
Analysis showed that only one salt was obtained from all these mixtures—the same as that obtained by Gräfinghoff. The salt is colorless when pure, but gradually becomes colored when exposed to the air. It gives off water and takes it up again, according to the temperature and hygroscopic state of the atmosphere. Solutions of the salt easily become supersaturated, and, in strong solutions, the salt crystallizes out in long, concentrically grouped plates, as described by Bibanow. The plates are striated, so that they have a sort of hour-glass appearance. They lose all their water over sulphuric acid, and can be heated in the air-bath to 120° without decomposing. When heated high enough, the salt melts to a brown liquid from which toluidine hydrochloride sublimes. As the salt loses water easily, it must be pressed between filter-paper, powdered, and not allowed to lie long in the air before analysis.

0.2775 gram salt lost 0.0024 gram water.

0.2021 gram salt gave 0.0359 gram ZnO and 0.2539 gram AgCl.

0.331 gram salt gave 0.0595 gram ZnO and 0.4171 gram AgCl.

| | Calculated for $ZnCl_2.2C_6H_4\left\langle\begin{matrix}CH_3\ 2H_2O\\ NH_3Cl\end{matrix}\right.$ | Found.<br>I. | II. | III. |
|---|---|---|---|---|
| Zn | 14.42 | .... | 14.26 | 14.33 |
| Cl | 30.86 | .... | 31.06 | 31.16 |
| $H_2O$ | 7.83 | 8.07 | .... | .... |

*Dimetatoluidine Chlorozincate*,  $ZnCl_2.2C_6H_4\left\langle\begin{matrix}CH_3\\ NH_3Cl\end{matrix}\right.$ .—This salt is formed when the constituents are brought together in the molecular proportions 3 : 1, 2 : 1. It forms fine, silken needles, which are extremely soluble in water. They cannot be washed, but must be sucked dry on the filter-pump and pressed between filter-paper. Owing to the nature of the crystals and their great solubility, it is very difficult to get a specimen of the salt pure enough to give sharp analytical results. The results are not as good as could be desired, but they are close enough to show that the compound has the formula given above.

0.0941 gram salt gave 0.0187 gram ZnO and 0.03187 gram Cl.

0.1917 gram salt gave 0.0377 gram ZnO and 0.2568 gram AgCl.

| | Calculated for $ZnCl_2.2C_6H_4\left\langle{}^{CH_3}_{NH_3Cl}\right.$. | Found. I. | II. |
|---|---|---|---|
| Zn | 15.42 | 15.95 | 15.8 |
| Cl | 33.48 | 33.87 | 33.13 |

These results were from different specimens.

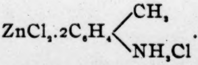
*Trimetatoluidine Chlorozincate*, $ZnCl_2.3C_6H_4\left\langle{}^{CH_3}_{NH_3Cl}\right.$.–Mixtures of zinc chloride and metatoluidine hydrochloride were made in aqueous solution in the proportions of 1 : 1, 1 : 2, 1 : 3, 1 : 4. All these gave the same double salt, the trimetatoluidine chlorozincate. The solutions soon assume a purple color, and the crystals are nearly always colored. When pure, they are colorless. The salt crystallizes in fine needles, which grow in radiating tufts and are not as soluble as the ditoluidine salts, but still are too soluble to be washed with water, and must be sucked dry and pressed between drying-paper. In this way they are obtained in good condition for analysis.

0.1394 gram salt gave 0.0201 gram ZnO and 0.1751 gram AgCl.

0.1929 gram salt gave 0.028 gram ZnO and 0.2426 gram AgCl.

0.2225 gram salt gave 0.0316 gram ZnO and 0.278 gram AgCl.

| | Calculated for $ZnCl_2.3C_6H_4\left\langle{}^{CH_3}_{NH_3.Cl}\right.$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Zn | 11.5 | 11.57 | 11.65 | 11.4 |
| Cl | 31.24 | 31.06 | 31.14 | 30.92 |

*Diparatoluidine Chlorozincate*,  $\mathrm{ZnCl_2.2C_6H_4}\left\langle\begin{array}{l}\mathrm{CH_3}\\\mathrm{NH_3Cl}\end{array}\right.$.—This salt was referred to under the corresponding orthotoluidine salt. Gräfinghoff said he prepared this at the same time that he made the ortho salt. He did not give any analysis nor did he state whether only one salt could be formed or more than one. There are two para salts, while only one ortho salt could be made.

Diparatoluidine chlorozincate is formed when zinc chloride and toluidine hydrochloride are mixed in the proportions 3 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3. The solutions were heated to boiling and made slightly acid. The salt crystallizes in colorless plates, which form a matted mass.

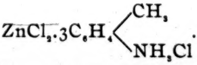
The solutions color very slowly. They cannot be purified by boiling with boneblack as they become colored more, to a deep purple. The crystals have various forms, sometimes triangular plates, sometimes triangular plates with the angles truncated.

The salt is easily soluble in cold water. It is stable in the air, and does not change color.

0.2567 gram salt gave 0.0489 gram ZnO and 0.3482 gram AgCl.

0.2743 gram salt gave 0.0524 gram ZnO and 0.3709 gram AgCl.

| | Calculated for $\mathrm{ZnCl_2.2C_6H_4}\left\langle\begin{array}{l}\mathrm{CH_3}\\\mathrm{NH_3Cl}\end{array}\right.$ | Found. I. | Found. II. |
|---|---|---|---|
| Zn | 15.42 | 15.3 | 15.37 |
| Cl | 33.48 | 33.54 | 33.44 |

*Triparatoluidine Chlorozincate*,  $\mathrm{ZnCl_2.3C_6H_4}\left\langle\begin{array}{l}\mathrm{CH_3}\\\mathrm{NH_3Cl}\end{array}\right.$.—This salt is formed when zinc chloride and paratoluidine hydrochloride are brought together in water solutions in the proportions 1 : 3, 1 : 4. The 1 : 4 mixture deposits the organic halide first. Sometimes the ditoluidine salt is formed in the 1 : 3 mixture. There is this tendency at low temperatures. At a slightly elevated temperature only the 1 : 3 salt is formed.

The compound crystallizes well, apparently in the triclinic system, and resembles albite crystals in outline. The forms are oP, $\bar{P}'\infty$, $\infty\,{}_{1}'P$, $\infty\,{}_{1}'P$, $\breve{\infty}P\infty$.

0.191 gram salt gave 0.0263 gram ZnO and 0.2406 gram AgCl.

0.2483 gram salt gave 0.0354 gram ZnO and 0.315 gram AgCl.

| | Calculated for | Found. | |
|---|---|---|---|
| | $ZnCl_2.3C_6H_4\left\langle\begin{matrix}CH_3\\NH_2Cl\end{matrix}\right.$. | I. | II. |
| Zn | 11.50 | 11.05 | 11.45 |
| Cl | 31.24 | 31.15 | 31.37 |

## *Double Bromides.*

*Dianiline Bromozincate*, $ZnBr_2.2C_6H_5NH_3Br.H_2O$.—Aniline hydrobromide behaves a little differently from the corresponding chloride, in that it separates out as such from mixtures in which the proportion of aniline hydrobromide to zinc bromide is greater than 2 : 1. A 3 : 1 mixture could not be made as in the case of the chloride. Addition of hydrobromic acid caused a still greater separation of the organic halide. Only one double salt could be obtained from all the different mixtures. It seemed to be best formed in a 1 : 1 solution. Sometimes a solution of one molecule of zinc bromide to two molecules of organic halide would deposit the organic halide along with the double salt. The salt crystallizes in thick prismatic plates resembling those of the corresponding double chloride, and probably belonging to the same system.

The solutions remain colorless, differing again in this respect from those of the corresponding chloride. The salt cannot be recrystallized from water, as aniline hydrobromide separates out. It is easily soluble in cold water. It loses its water when heated and does not decompose at 110°.

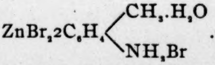
0.2452 gram salt gave 0.0345 gram ZnO and 0.3112 gram AgBr.

0.2249 gram salt gave 0.0318 gram ZnO.

0.2609 gram salt gave 0.3315 gram AgBr.

0.1758 gram salt lost 0.0052 gram $H_2O$.

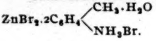
| | Calculated for | Found. | | | |
|---|---|---|---|---|---|
| | $ZnBr_2.2C_6H_5NH_3Br.H_2O$. | I. | II. | III. | IV. |
| Zn | 11.02 | 11.30 | 11.35 | .... | .... |
| Br | 54.19 | 54.00 | .... | 54.06 | .... |
| $H_2O$ | 3.05 | .... | .... | .... | 3.24 |

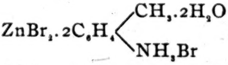
*Diorthotoluidine Bromozincate,*  $ZnBr_2 2C_6H_4<\begin{matrix}CH_3.H_2O\\NH_3Br\end{matrix}$.—
Orthotoluidine hydrobromide is like the chloride in its behavior towards zinc bromide ; that is, it does not separate out as such from mixtures in which it is present in excess, as the aniline hydrobromide does. Mixtures were made in many proportions, but only one salt could be obtained. The solutions change color slowly. The salt forms large colorless prismatic plates, which can be recrystallized from water. It can be heated in the air-bath to 120° without decomposition, and when heated to 150° it begins to melt to a blue liquid, giving off vapors of toluidine hydrobromide. The salt is readily soluble in cold water.

0.2564 gram salt gave 0.0339 gram ZnO and 0.31 gram AgBr.

0.6305 gram salt gave 0.852 gram ZnO and 0.7963 gram AgBr.

0.3802 gram salt lost 0.0117 gram water.

| | Calculated for  $ZnBr_2.2C_6H_4<\begin{matrix}CH_3.H_2O\\NH_3Br.\end{matrix}$ | Found. I. | II. | III. |
|---|---|---|---|---|
| Zn | 10.52 | 10.56 | 10.82 | .... |
| Br | 51.7 | 51.45 | 51.82 | .... |
| $H_2O$ | 2.9 | .... | .... | 3.08 |

*Dimetatoluidine Bromozincate,*  $ZnBr_2.2C_6H_4<\begin{matrix}CH_3.2H_2O\\NH_3Br\end{matrix}$.—
This salt is formed in solutions which contain zinc bromide in excess, that is, in 3 : 1, 2 : 1, 1 : 1 solutions. The salt is with difficulty obtained in pure condition, as there is a strong tendency to the formation of a tritoluidine salt, to be described presently.

Sometimes in these mixtures one crop will be the ditoluidine salt, the next crop a tritoluidine salt, and the third a ditoluidine salt again. The ditoluidine salt forms long, thick, prismatic bars. The solution soon becomes colored, and the crystals are nearly always more or less colored.

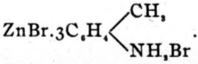
The compound loses its water in the air-bath and can be heated above 100° without decomposing.

0.2647 gram salt gave 0.0336 gram ZnO and 0.3128 gram AgBr.

0.2184 gram salt gave 0.0275 gram ZnO and 0.2581 gram AgBr.

0.2647 gram salt lost 0.0147 gram water.

| | Calculated for $ZnBr_2.2C_6H_4\left\langle\begin{matrix}CH_3.2H_2O\\NH_2Br\end{matrix}\right.$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Zn | 10.23 | 10.28 | 10.11 | .... |
| Br | 50.20 | 50.27 | 50.28 | .... |
| $H_2O$ | 5.64 | .... | .... | 5.59 |

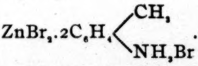
*Trimetatoluidine Bromozincate*, 
$ZnBr.3C_6H_4\left\langle\begin{matrix}CH_3\\NH_2Br\end{matrix}\right.$.—Of the two metatoluidine double salts this one is the more easily formed, being produced in solutions containing an excess of zinc bromide as well as in those which the toluidine hydrobromide is in excess. It crystallizes in long needles or prisms, for the most part colored purple. By pressing between filter-paper they are fit for analysis.

0.2291 gram salt gave 0.0237 gram ZnO and 0.11575 gram Br.

0.2663 gram salt gave 0.0289 gram ZnO and 0.1346 gram Br.

| | Calculated for $ZnBr_2.3C_6H_4\left\langle\begin{matrix}CH_3\\NH_2Br\end{matrix}\right.$. | Found. I. | II. |
|---|---|---|---|
| Zn | 8.26 | 8.30 | 8.47 |
| Br | 50.71 | 50.52 | 50.54 |

This salt is much less soluble in cold water than the corresponding chlorine salt. It was impossible to wash the latter without dissolving the crop of crystals, while the former can be washed clean on the filter-pump.

*Diparatoluidine Bromozincate*, 
$ZnBr_2.2C_6H_4\left\langle\begin{matrix}CH_3\\NH_2Br\end{matrix}\right.$.–When solutions of zinc bromide and paratoluidine hydrobromide are made in the proportions of 1 : 1, 1 : 2, 1 : 3, the paratoluidine hydrobromide crystallizes out without forming a double salt. Addition of hydrobromic acid causes more of the organic halide to separate out. In this respect the behavior is like

that of aniline hydrobromide. Mixtures containing zinc bromide in excess, for example 2 : 1, 3 : 1, yield a double salt, crystallizing in large, thin, shining, colorless leaves. These were filtered off, sucked dry, and pressed between filter-paper. When washed with water the crystals become opaque at once, evidently being decomposed. When an effort is made to recrystallize the salt from water, it is broken down, yielding crystals of paratoluidine hydrobromide. The salt is stable in the air and does not change color.

0.2122 gram salt gave 0.0283 gram ZnO.

0.1495 gram salt gave 0.1826 gram AgBr.

0.255 gram salt gave 0.0345 gram ZnO and 0.3107 gram AgBr.

0.2302 gram salt lost 0.0072 gram water.

| | Calculated for $ZnBr_2.2C_6H_4\left\langle\begin{array}{l}CH_3.H_2O\\NH_3Br\end{array}\right.$ | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Zn | 10.52 | 10.71 | .... | 10.85 | .... |
| Br | 51.70 | .... | 51.97 | 51.84 | .... |
| $H_2O$ | 2.9 | .... | .... | .... | 3.12 |

### *Double Ammonium Zinc Chlorides.*

As was stated at the beginning of this paper, the close relationship between ammonia and the organic bases made it desirable to investigate the double zinc ammonium chlorides, along with those of the organic bases, especially since a number of them are recorded, in regard to the existence of some of which a doubt may fairly be entertained. The following salts are recorded :

1. $ZnCl_2.2NH_4Cl.H_2O$. Schindler, Geiger's and Liebig's Mag., **36**, 43; Hautz, Ann. Chem. (Liebig), **66**, 287. The latter says he obtained the salt from one part ammonium and two parts zinc chloride.

2. $ZnCl_2.NH_4Cl.2H_2O$. Hautz, *loc. cit.* He mixed one part of each constituent and obtained this salt in large shining leaves, as he says.

3. $ZnCl_2.2NH_4Cl$. Rammelsberg. Ann. der phys. (Pogg.), **94**, 507; also Marignac, Ann. des Mines [5], **12**, 1.

4. $ZnCl_2.3NH_4Cl$. Marignac, *loc. cit.*

5. $ZnCl_2.NH_4Cl$. }
6. $ZnCl_2.4NH_4Cl$. } Dehérain, Bl. (1861), 51, says that

$ZnCl_2.NH_3$, $ZnCl_2.2NH_4$, and $ZnCl_2.NH_3$, when dissolved in hydrochloric acid, yield corresponding double chlorides.

$$\left.\begin{array}{l}\text{7. } ZnCl_2.6NH_4Cl.\tfrac{2}{3}H_2O.\\ \text{8. } ZnCl_2.3NH_4Cl.H_2O.\end{array}\right\}\text{ Berthelot and André, Ann. chim.}$$

phys. (6), **11**, 294–310. These chemists mention the existence of these two salts but do not state how they were obtained.

By working under various conditions, I was able to obtain only two double salts; *viz.*, Nos. 3 and 4 in the list above, which were also obtained by Marignac. He did not make a thorough study, but made a mixture in only one molecular proportion. As these salts were completely described by Marignac, I cannot do better than to give his own words. He says, "In his treatise on crystallographical chemistry, Rammelsberg describes the crystal forms of this salt, (*i. e.*, No. 3) to which he attributes the formula $ZnCl_2.2NH_4Cl$. An earlier analysis by Schindler made it appear to contain an equivalent of water. And it is to be noticed that the crystals described by Rammelsberg may be regarded as isomorphous with the stannous ammonium chloride described by the same chemist, of which he represents the composition by the formula $SnCl_2.2NH_4Cl.H_2O$. These considerations have induced me to undertake again the examination of these salts. The results have not answered to what I supposed, but they are not the less curious. They prove, in effect, the existence of two double salts, both anhydrous, and represented by the formulas (see 3 and 4 above). What is most singular is that these two salts, perfectly distinct as regards their appearance and their faces, have forms which can be derived from one another. However, one cannot call them isomorphous, since they do not mix in anywise in crystallizing, and there is no passage from the one to the other, although they are formed sometimes simultaneously in the same beaker."

Marignac calls $ZnCl_2.2NH_4Cl$ the laminated salt and $ZnCl_2.3NH_4Cl$ the prismatic salt. He dried the salts in all cases at 100°, at which temperature they preserved their transparency and lost only a trace of hygroscopic water. The prismatic crystals are right rhombohedral prisms.

*Diammonium Chlorozincate*, $ZnCl_2.2NH_4Cl$.—Mixtures of zinc chloride and ammonium chloride were made in the molecular proportions of 3 : 1, 2 : 1, 1 : 1, 1 : 2. The same salt was obtained from all of them, the laminated salt of Marignac. It forms large shining plates. Sometimes a 1 : 2 mixture gave the 1 : 3 salt at first, and the 1 : 2 salt in later crops. The mixtures were neutral or slightly acid.

0.2125 gram salt gave 0.0711 gram ZnO and 0.5036 gram AgCl.

0.1891 gram salt gave 0.0632 gram ZnO.

0.2456 gram salt gave 0.5776 gram AgCl.

| | Calculated for $ZnCl_2.2NH_4Cl$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Zn | 26.83 | 26.86 | 26.84 | .... |
| Cl | 58.32 | 58.60 | .... | 58.16 |

*Triammonium Chlorozincate*, $ZnCl_2.3NH_4Cl$.—Solutions of zinc chloride and ammonium chloride, in the proportions of 1 : 3, 1 : 4, 1 : 6, gave only the 1 : 3 salt. In the 1 : 6 solution, ammonium chloride crystallized out first.

0.1546 gram salt gave 0.0424 gram ZnO and 0.3759 gram AgCl.

0.4685 gram salt gave 0.1272 gram ZnO and 1.1267 grams AgCl.

| | Calculated for $ZnCl_2.3NH_4Cl$. | Found. I. | II. |
|---|---|---|---|
| Zn | 22.00 | 22.02 | 21.80 |
| Cl | 59.76 | 60.13 | 59.47 |

Solutions of zinc chloride and ammonium chloride were made in the proportions of 1 : 1 and 1 : 4, in concentrated hydrochloric acid in order to see if the strong acid would cause the formation of salts different from those just described. The first crop of crystals from the 1 : 1 solution was the 1 : 3 salt of Marignac, as was shown by their appearance and analysis. The other crops were composed of plates which proved to be the 1 : 2 salt. The 1 : 4 solution gave the 1 : 3 salt.

Dehérain says that when $ZnCl_2.NH_3$ and $ZnCl_2.4NH_3$ are dissolved in hydrochloric acid, corresponding double salts are formed. According to Kane,[1] $ZnCl_2.4NH_3.H_2O$ is formed when concentrated ammonia is added to a hot concentrated solution of zinc chloride, until the precipitate first formed is redissolved. On cooling, the salt is said to separate out in small brilliant plates with pearly luster. According to Marignac,[1] $ZnCl_2.2NH_3$ is often formed at once when the two solutions are brought together, as described by Kane. Kane says that, on further evaporation of the solution after removing the first crop of crystals, $ZnCl_2.2NH_3.\frac{1}{2}H_2O$ crystallizes out in radiating groups of square prisms of a brilliant vitreous luster. $ZnCl_2.NH_3$ is obtained, according to Kane, by heating $ZnCl_2.4NH_3.H_2O$ or $ZnCl_2.2NH_3.\frac{1}{2}H_2O$, ammonia and water being given off and a gummy mass remaining.

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[1] Ann. Chem. (Liebig), [2], 72, 290.

Following Kane's directions, as Dehérain also did, a compound was obtained, the analysis of which gave results agreeing fairly well with the formula $ZnCl_2.4NH_3.H_2O$. The determination of zinc gave a figure which was less than the theoretical per cent. by 1.6 per cent. Some of the compound was dissolved in hydrochloric acid and allowed to crystallize. Small prismatic crystals were obtained that resembled, in all respects, the 1 : 3 salt described by Marignac. A determination of zinc was made, 0.2397 gram giving 0.0647 gram ZnO, *i. e.*, 21.74 per cent., the theoretical being 22.00 per cent. for the 1 : 3 salt.

On heating the rest of the compound, $ZnCl_2.4NH_3.H_2O$, ammonia was given off and a gummy mass was left, as described by Kane. This was dissolved in hydrochloric acid and allowed to crystallize. Thin, shining plates were formed looking exactly like the 1 : 2 salt already described. It seems then, that dissolving these compounds in hydrochloric acid is equivalent to making solutions of zinc chloride and ammonium chloride in the proportions of 1 : 4 and 1 : 1, and we have seen that the former solution yields a 1 : 3 salt, while the latter yields a 1 : 2 salt.

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[1] Ann. des Mines [5], **12**, 1.

Contributions from the Chemical Laboratory of Purdue University.

# SULPHONATION OF THE PARAFFINS.

By R. A. Worstall.

The comparative ease with which the paraffins can be nitrated, as set forth in a previous communication,[1] suggested the idea that under proper conditions they might also be capable of direct sulphonation. So far as I am aware, there is no recorded instance of such sulphonation having been accomplished. It is stated by all authorities, and is probably accepted without question, that neither sulphuric acid nor its anhydride will react with aliphatic hydrocarbons.

A few preliminary experiments with octane and sulphuric acid demonstrated to my own satisfaction that a reaction certainly took place between the two. But for some time all such experiments led to no definite results, simply because it was assumed that the reaction would take place, if at all, only with great difficulty, and the method of sulphonation at first employed was far too vigorous. It was not until it was recognized that this reaction, like the nitration, is in reality easily brought about, that any progress was made.

In the preliminary experiments, for which octane was employed, the sulphonation was attempted by boiling the hydrocarbon with fuming sulphuric acid. While it was evident, from the blackening of the acid and the evolution of sulphur dioxide, that a reaction was taking place, nothing but a tarry mass was left in the flask, and from it no sulphonic acids could be obtained. It was subsequently found that it is necessary to heat the two only to the boiling-point of the hydrocarbon, or even lower, and that in fact any considerable increase in temperature above this point destroys the sulphonic acids.

Comparative experiments were tried with octane, using sulphuric acid of specific gravity 1.84, and the fuming acid, both in sealed tubes and open flasks. While in either case both acids react to form sulphonic acids, the best results and the largest yield were obtained by using successive small portions of fuming sulphuric acid in an open flask with return-condenser, keeping the contents near the boiling-point of the hydrocarbon, and shaking vigorously. By this method, apparently only the monosulphonic acids were formed, whereas, as will be seen later, the action of sulphuric anhydride alone gives rise to the formation of disulphonic acids.

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[1] This Journal, 20, 202.

The hydrocarbons which have been employed are the normal paraffins, hexane, heptane, and octane.[1] Each hydrocarbon was the residue left after reducing 200 or 300 grams of the original hydrocarbon by nitration to 40 or 50 grams. This residue in each case was distilled, boiled with sodium for a day to free it from nitro-compounds, redistilled, the distillate washed with cold fuming sulphuric acid, and with caustic soda, dried, and again distilled. The boiling-points were sharp and constant, and the treatment which each had undergone would seem to exclude any possibility of the presence of hydrocarbons other than the paraffins.

### *Hexane*, $C_6H_{14}$.

The normal hexane employed boiled at 68°–69° (uncorr.), and its specific gravity was 0.6860 at $\frac{20^\circ}{20^\circ}$. For the production of the monosulphonic acid the hydrocarbon was heated on the steam-bath with successive small portions of fuming sulphuric acid in a flask with return-condenser. The flask was shaken vigorously throughout the reaction, the acid layer becoming deep brown, and considerable sulphur dioxide being evolved. By repeating the treatment with the residual hydrocarbon, a yield of from 30 to 40 per cent. of the theoretical was obtained, the rest of the hydrocarbon being oxidized to carbon dioxide and water.

The mixed acids were diluted with water and the brown solution thus obtained neutralized with barium carbonate. The filtrate was boiled to decompose any acid carbonate of barium, filtered again, and the filtrate evaporated to dryness. The salts of the sulphonic acids examined were so extremely soluble in water that no well-defined crystals could be obtained from aqueous solution, and no better results were obtained from dilute alcoholic solutions. And on account of lack of time the salts have been purified, as well as possible, by other means and the anhydrous salt employed.

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[1] For the original hydrocarbons I am indebted to Dr. C. F. Mabery.

*Barium Hexylsulphonate*, $(C_6H_{13}SO_3)_2Ba$. — The barium compound as obtained consisted of brown plates. By boiling with animal charcoal, filtering, and evaporating to dryness, the brown color is removed, leaving the salt light-yellow. Analysis gave the following results:

0.0736 gram gave 0.0368 gram $BaSO_4$ (for barium).
0.1025 gram gave 0.1035 gram $BaSO_4$ (for sulphur).

| | Calculated for $(C_6H_{13}SO_3)_2Ba$. | Found. |
|---|---|---|
| Ba | 29.33 | 29.48 |
| S | 13.71 | 13.85 |

Barium was determined by igniting with sulphuric acid to barium sulphate. Sulphur by fusion with sodium carbonate and potassium nitrate and the estimation of sulphuric acid in the water solution of the fusion.

Barium hexylsulphonate is a neutral salt, light-yellow in color, extremely soluble in water, insoluble in alcohol, ether, and other organic solvents. It is precipitated from its aqueous solution in an amorphous form by alcohol.

*Lead Hexylsulphonate*, $(C_6H_{13}SO_3)_2Pb$.—The barium salt was converted into that of lead by dissolving in water, precipitating the barium with a slight excess of sulphuric acid, neutralizing the filtrate with lead carbonate, filtering, and evaporating to dryness. Analysis of the salt gave the following results:

0.0844 gram gave 0.0477 gram $PbSO_4$.
0.1393 gram gave 0.1211 gram $BaSO_4$.

| | Calculated for $(C_6H_{13}SO_3)_2Pb$. | Found. |
|---|---|---|
| Pb | 38.55 | 38.61 |
| S | 11.92 | 11.91 |

The lead salt resembles the barium salt in all its properties.

*Hexylsulphonic Acid*, $C_6H_{13}SO_3H$.—The lead salt was dissolved in water and the lead removed by hydrogen sulphide. The filtered solution was then evaporated to dryness, again dissolved in water, and filtered to remove traces of lead sulphide, and again evaporated to dryness. The acid was then dried at 105° for an hour.

0.0706 gram acid gave 0.1006 gram $BaSO_4$.

| | Calculated for $C_6H_{13}SO_3H$. | Found. |
|---|---|---|
| S | 19.27 | 19.54 |

Hexylsulphonic acid is a thick liquid, light-brown in color. It is readily soluble in alcohol and water, insoluble in ether, chloroform, etc.; soluble in hot benzol, and is at once extracted by water from the latter solution. It could not be crystallized. It has an intense acid taste and strong acid reaction, all of its salts appearing to be soluble in water. The amount obtained was so small that nothing further could be done in the way of identification.

### *Action of Sulphuric Anhydride.*

To determine the action of sulphuric anhydride upon hexane, the hydrocarbon was placed in a flask fitted with a two-hole rubber stopper, through which passed a reflux-condenser and a gas-delivery tube leading just above the surface of the hydrocarbon.

This oil was set to boiling upon the steam-bath, and a stream of sulphur trioxide, made by distilling fuming sulphuric acid, was passed in through the delivery-tube. A reaction took place at once with the production of heavy brown vapors which condensed to a liquid upon the walls of the flask, while from the evolution of sulphurous acid it was evident that oxidation was also resulting.

After passing in the anhydride for a short time, the flask was cooled, and the unchanged hydrocarbon poured out. The sulphonic acid was washed out with water, and the process repeated with the residual hydrocarbon, the best results being obtained in this way. Thirty grams of hexane were treated with the anhydride for ten minutes. The loss in weight of the hydrocarbon was 6 grams, and from this 6 grams of barium salt was obtained. The residue of 25 grams hexane was again treated in the same way for twenty-five minutes, when it lost 13 grams and yielded 11 grams of the barium salt. By continuing the sulphonation in this way, the yield of disulphonic acid was about 40 per cent. of the theoretical, the rest of the hydrocarbon being completely oxidized.

*Barium Hexyldisulphonate*, $C_6H_{12}(SO_3)_2Ba$.—The solution of the sulphonic acid as above obtained, was converted into the barium salt by means of barium carbonate. This salt was purified with bone-black, and dried for an hour at 105°.

0.1014 gram gave 0.0615 gram $BaSO_4$ (for barium).

0.1370 gram gave 0.1625 gram $BaSO_4$ (for sulphur).

| | Calculated for $C_6H_{12}(SO_3)_2Ba$. | Found. |
|---|---|---|
| Ba | 35.95 | 35.71 |
| S | 16.80 | 16.36 |

In its solubilities and general properties this compound closely resembles the barium salt of the monosulphonic acid. It is golden-yellow, soluble in water, and quite deliquescent, absorbing moisture rapidly from the air.

*Lead Hexyldisulphonate*, $C_6H_{12}(SO_3)_2Pb$.—The barium salt was converted into the lead salt in the usual way. The latter, after drying for an hour at 105°, gave the following results upon analysis:

0.1326 gram gave 0.0882 gram $PbSO_4$.

0.1244 gram gave 0.1296 gram $BaSO_4$.

By combustion with lead chromate, 0.1512 gram gave 0.0870 gram $CO_2$; and 0.0347 gram $H_2O$.

| | Calculated for $C_6H_{12}(SO_3)_2Pb$. | Found. |
|---|---|---|
| C | 15.96 | 15.69 |
| H | 2.66 | 2.56 |
| S | 14.19 | 14.27 |
| Pb | 45.89 | 45.45 |

Golden-yellow salt, with a slight acid reaction; extremely soluble in water, rapidly absorbing moisture from the air; insoluble in alcohol, ether, etc.

*Hexyldisulphonic Acid*, $C_6H_{12}(SO_3H)_2$.—The free acid was obtained from the lead salt by removing the lead with hydrogen sulphide. The filtrate was evaporated to dryness, the residue extracted with hot alcohol, filtered, and the alcoholic extract evaporated to dryness. Analysis gave the following results:

0.0470 gram gave 0.0895 gram $BaSO_4$.

By combustion with lead chromate, 0.1356 gram gave 0.1449 gram $CO_2$; and 0.0645 gram $H_2O$.

| | Calculated for $C_6H_{12}(SO_3H)_2$. | Found. |
|---|---|---|
| C | 29.27 | 29.14 |
| H | 5.69 | 5.29 |
| S | 26.01 | 26.17 |

Hexyldisulphonic acid is a thick sirup that gave no signs of crystallizing; brown in color; extremely soluble in water, absorbing moisture rapidly from the air; soluble in hot benzol and alcohol; insoluble in petroleum, ether, etc.; strong acid reaction and sharp taste. All its salts appear to be soluble in water.

### *Heptane*, $C_7H_{16}$.

The heptane employed was the normal hydrocarbon boiling at 98°–99°, specific gravity 0.6980, at $\frac{20°}{20°}$. For the formation of the monosulphonic acid the hydrocarbon was heated on the steam-bath with successive small portions of fuming sulphuric acid in a flask with return-condenser. The flask was well shaken during the reaction, the acid layer becoming deep brown. Thirty grams of heptane by warming with four successive portions of fuming acid lost 15 grams and yielded 12 grams of the barium sulphonate. By continuing the sulphonation with the residue, the yield amounted to about the same as for hexane—that is, about 40 per cent. of the theoretical. The mixed acids were diluted with water, giving a green solution which, when neutralized with barium carbonate, became light-brown.

*Barium Heptylsulphonate*, $(C_7H_{15}SO_3)_2Ba$. — The barium salt was purified by boiling with bone-black, filtering, and evaporating to dryness. Analysis gave the following results:

0.2070 gram gave 0.0961 gram $BaSO_4$ (for barium).
0.0923 gram gave 0.0877 gram $BaSO_4$ (for sulphur).

| | Calculated for $(C_7H_{15}SO_3)_2Ba$. | Found. |
|---|---|---|
| Ba | 27.68 | 27.35 |
| S | 12.93 | 13.01 |

Barium heptylsulphonate resembles the corresponding derivative of hexane in its properties.

*Lead Heptylsulphonate*, $(C_7H_{15}SO_3)_2Pb$.—The barium salt was converted into that of lead in the usual manner and the latter analyzed.

0.1562 gram gave 0.0831 gram $PbSO_4$.
0.1113 gram gave 0.0923 gram $BaSO_4$.

| | Calculated for $(C_7H_{15}SO_3)_2Pb$. | Found. |
|---|---|---|
| Pb | 36.64 | 36.40 |
| S | 11.33 | 11.38 |

It is a light-yellow salt, very soluble in water, insoluble in alcohol, etc.; resembling the barium compound closely.

*Heptylsulphonic Acid*, $C_7H_{15}SO_3H$.—The free acid was obtained from the lead salt by means of hydrogen sulphide. After purifying and drying at 105°, a sulphur determination was made.

0.3191 gram gave 0.4178 gram $BaSO_4$.

| | Calculated for $C_7H_{15}SO_3H$. | Found. |
|---|---|---|
| S | 17.77 | 17.96 |

The free sulphonic acid is a thick brown sirup, that could not be crystallized; soluble in alcohol; extremely soluble in water; insoluble in ether, etc. Upon warming with phosphorus pentachloride a reaction took place readily with the evolution of hydrochloric acid. From the product of the reaction an oily liquid was obtained, insoluble in water, apparently a sulphonchloride. This was dissolved in alcohol and the solution saturated with dry ammonia gas. In this way a sulphonamide was apparently produced. Determination of sulphur and nitrogen showed it to be an impure heptylsulphonamide, but not a sufficient amount was obtained for further examination.

## *Action of Sulphuric Anhydride.*

When heptane was set to boiling gently upon a steam-bath, and sulphur trioxide passed in, in the manner already described for hexane, a vigorous reaction took place. Heavy brown vapors were formed, condensing to a liquid on the walls of the flask, consisting of the disulphonic acid. At the same time considerable sulphur dioxide was evolved, in consequence of the oxidation of part of the hydrocarbon.

*Barium Heptyldisulphonate*, $C_7H_{14}(SO_3)_2Ba$.—The sulphonic acid was isolated by diluting with water and neutralizing with barium carbonate. The barium salt thus obtained, after purifying with bone-black and drying at 105°, was analyzed.

0.1776 gram gave 0.1040 gram $BaSO_4$ (for barium).

0.1330 gram gave 0.1525 gran $BaSO_4$ (for sulphur).

| | Calculated for $C_7H_{14}(SO_3)_2Ba$. | Found. |
|---|---|---|
| Ba | 34.68 | 34.44 |
| S | 16.20 | 15.81 |

It is a light-yellow salt of neutral reaction, resembling in its solubilities and other properties the corresponding derivative of hexane.

*Lead Heptyldisulphonate*, $C_7H_{14}(SO_3)_2Pb$.—The barium salt was converted into that of lead in the usual manner and the latter analyzed.

0.1395 gram gave 0.0901 gram $PbSO_4$.

0.1034 gram gave 0.1029 gram $BaSO_4$.

By combustion with lead chromate, 0.2646 gram gave 0.1743 gram $CO_2$, and 0.0678 gram $H_2O$.

| | Calculated for $C_7H_{14}(SO_3)_2Pb$. | Found. |
|---|---|---|
| C | 18.06 | 17.96 |
| H | 3.01 | 2.85 |
| S | 13.76 | 13.63 |
| Pb | 44.51 | 44.20 |

It is a light-yellow salt, quite deliquescent; extremely soluble in water; insoluble in alcohol, ether, etc.; slight acid reaction in aqueous solution.

*Heptyldisulphonic Acid*, $C_7H_{14}(SO_3H)_2$.—The free acid was obtained from the lead salt by removing the lead with hydrogen sulphide. The aqueous solution of the acid was evaporated to dryness, extracted with alcohol, filtered, and again evaporated to dryness. After drying for an hour at 105° the acid was analyzed.

0.0913 gram gave 0.1608 gram $BaSO_4$.

By combustion with lead chromate, 0.1486 gram gave 0.1738 gram $CO_2$, and 0.0808 gram $H_2O$.

| | Calculated for $C_7H_{14}(SO_3H)_2$. | Found. |
|---|---|---|
| C | 32.30 | 31.90 |
| H | 6.15 | 6.05 |
| S | 24.61 | 24.21 |

Heptyldisulphonic acid is a pasty, dark-brown mass. It could not be solidified or crystallized by standing. It is extremely soluble in water, rapidly absorbing sufficient moisture from the air to become liquid; soluble in hot alcohol and benzol; insoluble in ether, petroleum ether, etc.; strong acid reaction and intense acid taste. All its salts are soluble in water.

### *Octane*, $C_8H_{18}$.

The normal octane employed boiled at 124°–125° (uncorr.), and its specific gravity was 0.7123 at $\frac{20°}{20°}$.

The monosulphonic acid was prepared by heating the hydrocarbon with about five times its weight of fuming sulphuric acid in a flask with return-condenser. The flask was vigorously shaken and the temperature was not allowed to exceed 125°. The acid layer became deep-brown and considerable sulphur dioxide was evolved. In one case, 15 grams octane, when treated in this manner three times with fresh portions of the fuming acid, lost 7 grams, and yielded 6 grams of the barium sulphonate. By repeating the sulphonation with the residual hydrocarbon a yield of from 30 to 40 per cent. of the theoretical was obtained.

*Barium Octylsulphonate*, $(C_8H_{17}SO_3)_2Ba$.—The mixed acids were diluted with water and neutralized with barium carbonate. The barium salt thus obtained was purified with bone-black, dried at 105°, and analyzed.

0.2808 gram gave 0.1254 gram $BaSO_4$ (for barium).
0.2128 gram gave 0.1925 gram $BaSO_4$ (for sulphur).

| | Calculated for $(C_8H_{17}SO_3)_2Ba$. | Found. |
|---|---|---|
| Ba | 26.19 | 26.25 |
| S | 12.26 | 12.44 |

It is a light-yellow salt, resembling in solubilities and general properties the corresponding derivatives of heptane and hexane.

*Lead Octylsulphonate*, $(C_8H_{17}SO_3)_2Pb$.—The barium salt was converted into the lead salt and the latter, after drying at 105°, was analyzed.

0.1652 gram gave 0.0850 gram $PbSO_4$.
0.1628 gram gave 0.1310 gram $BaSO_4$.

| | Calculated for $(C_8H_{17}SO_3)_2Pb$. | Found. |
|---|---|---|
| Pb | 34.91 | 35.05 |
| S | 10.79 | 10.93 |

The lead salt resembled the barium salt in appearance and properties.

*Octylsulphonic Acid*, $C_8H_{17}SO_3H$.—The free acid was obtained from the lead salt by removing the lead with hydrogen sulphide. The acid was dried at 105°.

0.1041 gram gave 0.1277 gram $BaSO_4$.

| | Calculated for $C_8H_{17}SO_3H$. | Found. |
|---|---|---|
| S | 16.49 | 16.71 |

Octylsulphonic acid is a thick sirup, very soluble in water, soluble in alcohol, insoluble in petroleum ether, carbon disulphide, etc. It has a strong acid reaction. All its salts are soluble in water.

### *Action of Sulphuric Anhydride.*

When sulphur trioxide is passed into gently boiling octane in the manner described for hexane, a similar reaction occurs with the formation of a disulphonic acid. Considerable oxidation results at the same time, and sulphur dioxide is formed.

*Octyldisulphonic Acid*, $C_8H_{16}(SO_3H)_2$.—The brown liquid produced by the action of the anhydride was diluted with water, neutralized with lead carbonate, and the free acid obtained from the lead salt by means of hydrogen sulphide. The acid solution was evaporated to dryness, extracted with hot alcohol, and the alcoholic solution evaporated to dryness. Analysis of the acid gave the following results :

By combustion with lead chromate, 0.1128 gram gave 0.1416 gram $CO_2$, and 0.0664 gram $H_2O$.

| | Calculated for $C_8H_{16}(SO_3H)_2$. | Found. |
|---|---|---|
| C | 34.66 | 34.24 |
| H | 6.49 | 6.38 |

Octyldisulphonic acid is a brown, pasty mass, very deliquescent, extremely soluble in water, slowly soluble in alcohol and hot benzol ; insoluble in ether, etc.; strong acid reaction. All its salts are soluble in water.

When sulphuric anhydride was passed into the boiling hydrocarbons in the manner described, there was formed in each case, in addition to the sulphonic acids, a dark-brown solid, insoluble in water. When the solution was diluted with water, the latter compound was filtered off, washed with hot water, and dried. In the case of hexane and heptane this product amounted to only a very small fraction of a per cent., the total amount obtained from each being about a tenth of a gram. From octane, however, the amount obtained amounted to several per cent. These compounds were, after drying, brittle, lustrous solids of a dark-brown color, insoluble in water and all organic solvents ; readily oxidized by heating with strong nitric acid. They were at first thought to be sulphones, but analysis showed that this was not the case. The analytical results obtained were as follows :

| | 1. (From $C_6H_{14}$). | 2. (From $C_7H_{16}$). | 3. (from $C_8H_{18}$). |
|---|---|---|---|
| C | 47.16 | 49.51 | 51.90 |
| H | 3.78 | 4.08 | 4.50 |
| S | .... | .... | 11.44 |

These results would seem to show that the products were definite compounds of a regular series, high in oxygen (possibly oxysulphones). But from the very small quantities obtained and their indifference to all reagents, their identity could not be established.

From the results of the investigation, the following conclusions may be drawn :

1. Aliphatic hydrocarbons, as well as the aromatic, are readily capable of direct sulphonation.

2. Regulation of temperature is essential to the proper control of the reaction. Cold fuming sulphuric acid is without perceptible action upon the pure hydrocarbon. But if the temperature employed be too high, the sulphonic acids, which are at first formed, are destroyed. The correct temperature to employ would seem to be the boiling-point of the hydrocarbon.

3. Gentle methods of sulphonation, such as warming with fuming sulphuric acid, seem to yield only the monosulphonic acid, while more vigorous methods, as the use of sulphuric an-

hydride, result in the formation of disulphonic acids. It appeared occasionally, from the difficulty experienced in purifying the salts of the monosulphonic acid, that some disulphonic acid had been formed at the same time, even by the former method.

4. By the methods described yields of about 40 per cent. of the theoretical can be obtained, both of the mono- and of the disulphonic acids. The rest of the hydrocarbon is oxidized to carbon dioxide and water.

The preliminary results communicated in a former paper[1] in regard to the nitration of paraffins are being confirmed by a more complete and extended investigation of this reaction now in progress. Yields of mixed nitroparaffins have been obtained, amounting in the case of nonane to 70 per cent. of the theoretical, of octane to 55 per cent., and of heptane to 40 per cent. These results, in connection with those obtained by the sulphonation, certainly disprove the statements constantly met with, even in the latest text-books of organic chemistry, that aliphatic hydrocarbons differ from the aromatic hydrocarbons, in that the former are not capable of nitration by nitric acid, or of sulphonation by sulphuric acid.

Orndorff and Young[2] state that they found propane to be slowly absorbed by fuming sulphuric acid, the acid turning first red, then brown, and express surprise that propane, a member of the marsh gas series, should thus be absorbed. This statement, taken in connection with the peculiar fact that the three paraffins examined can be sulphonated ***at their boiling-points***, suggests that the example cited by Orndorff and Young was one of actual sulphonation. This investigation is therefore being extended to the behavior of the gaseous members of the aliphatic series towards fuming sulphuric acid.

LAFAYETTE, IND., May, 1898.

[1] *Loc. cit.*

[2] This JOURNAL, **15**, 261.

# THE FORMATION OF HYDRAZIDES BY THE ACTION OF PHENYLHYDRAZINE UPON ORGANIC ACIDS IN THE COLD.

BY VIRGIL L. LEIGHTON.

The phenylhydrazides of organic acids have been made by the following methods: Heating the acid or a solution of the acid with phenylhydrazine;[1] action of the base upon the chloride of the acid;[2] action of the sodium derivative of phenylhydrazine upon the chloride of the acid;[3] action of the base upon the amide of the acid;[4] treating the ester with phenylhydrazine;[5] and by the action of phenylhydrazine upon the acetylanhydride of the acid.[6]

It came under my observation that phenylhydrazine acetate on standing a few days at the ordinary temperature in a solution of acetic acid passed over into the hydrazide. As no observation of this kind appears to have been made before, other acids were tried, to determine if the reaction is general.

The course of procedure was, in the case of all liquid acids, first to make the salt by treating the acid with the calculated amount of phenylhydrazine, care being taken in all cases to avoid heating. The salt thus formed was dissolved in as little of the acid as possible, and the mixture allowed to stand at the ordinary temperature until the reaction seemed complete. A little water was then added (usually about four times the weight of the acid used), and the crystals filtered off. In this way the phenylhydrazides of formic, acetic, propionic, isobutyric, isocaproic, and heptoic acids have been made. This method will undoubtedly be of considerable advantage for obtaining the hydrazides of acids which cannot be heated.

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[1] Fischer: Ann. Chem. (Liebig), **190**, 29; and Ber. d. chem. Ges., **22**, 2728; Bülow: Ann. Chem. (Liebig, **236**, 134.

[2] Fischer: Ann. Chem. (Liebig), **190**, 125; Freund and Goldsmith: Ber. d. chem. Ges., **21**, 2456; Gattermann: *Ibid*, **25**, 1081.

[3] Michaelis and Schmidt: Ann. Chem. (Liebig), **252**, 301.

[4] Just: Ber. d. chem. Ges., **19**, 1201; Freund and Goldsmith: *Ibid*, **21**, 2461.

[5] Fischer: Ann. Chem. (Liebig). **190**, 131; Freund and Goldsmith: Ber. d. chem. Ges., **21**, 1241.

[6] Autenrieth: Ber. d. chem. Ges., **20**, 3187.

## *Experiments.*

*Formylphenylhydrazide.*[1]—Two grams of phenylhydrazine were dissolved in 2.4 grams of formic acid, care being taken to avoid heating. Crystals of formylphenylhydrazide began to appear after about one-half hour; after two hours the mass was nearly solid. It was allowed to stand twenty-four hours, then a little water was added; the crystals were separated and washed with water, whereby 1.8 grams were obtained (71.7 per cent. of the theory). Crystallized from alcohol, and dried in a vacuum over sulphuric acid, it melted at 144°–145° and gave, on analysis, the following results:

0.1746 gram of substance gave 0.3979 gram of carbon dioxide and 0.0982 gram of water.

|  | Calculated for $C_6H_5N_2H_2CHO$. | Found. |
|---|---|---|
| C | 61.77 | 61.91 |
| H | 5.88 | 6.26 |

*Acetylphenylhyrazide.*[2]—Two grams of phenylhydrazine were dissolved in 3.4 grams of acetic acid. Crystals began to appear after two days. It was allowed to stand two days longer, and water was then added; the crystals were separated by filtration, and washed with water. 1.7 grams were obtained (61.1 per cent. of the theory), which crystallized from dilute alcohol melted at 128° and agreed in properties with acetylphenylhydrazide. An attempt to form this compound by dissolving phenylhydrazine acetate in water and allowing the solution to stand at the ordinary temperature gave negative results.

*Propionylphenylhydrazide.*[3]—Two grams of phenylhydrazine were dissolved in 4 grams of propionic acid. On standing over night some crystals of propionylphenylhydrazide were formed. After five days, water was added, and the crystals were separated and washed with water. 2.6 grams were obtained (86.6 per cent. of the theory). Crystallized from alcohol it melted at 157°–158° (Freund and Goldsmith gave the melting-point as 157°–158°).

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[1] This compound was first made by Just: Ber. d. chem. Ges., **19**, 1201.

[2] First obtained by Fischer: Ann. Chem. (Liebig), **190**, 129.

[3] First made by Freund and Goldsmith: Ber. d. chem. Ges., **21**, 2461.

*Isobutyrylphenylhydrazide.*—To 1.4 grams of phenylhydrazine were added 4.5 grams of isobutyric acid. The mass began to crystallize after five days. Some hydrazide was formed before that time, as was shown by adding water to a small portion that had stood but three days, crystals separating at once. After standing seven days water was added, and 0.6 gram obtained (25 per cent. of the theory).

Isobutyrylphenylhydrazide is nearly insoluble in cold water, moderately soluble in cold, easily in hot alcohol. Crystallized from the latter it appears as slightly pink, rectangular tablets (sometimes hexagonal), melting at 142°–143°. The analysis gave the following results :

0.1211 gram of substance gave 0.2982 gram of carbon dioxide and 0.0884 gram of water.

| | Calculated for $C_6H_5N_2H_2COC_3H_7$. | Found. |
|---|---|---|
| C | 67.41 | 67.15 |
| H | 7.86 | 8.09 |

*Isohexylphenylhydrazide.*—0.4 gram of phenylhydrazine was dissolved in 2 grams of isocaproic (isobutylacetic) acid. Some hydrazide was deposited after twenty-four hours. It was allowed to stand five days, water was then added and 0.35 gram obtained (47.1 per cent. of the theory). It is nearly insoluble in cold water, soluble in alcohol, nearly insoluble in cold, easily in hot ligroïn, from which it crystallizes in thin transparent crystals, melting at 144°–145°. The analysis gave the following results :

0.1904 gram of substance gave 0.4887 gram of carbon dioxide and 0.1558 gram of water.

| | Calculated for $C_6H_5N_2H_2COC_5H_{11}$. | Found. |
|---|---|---|
| C | 70.24 | 69.99 |
| H | 8.78 | 9.10 |

*Heptylphenylhydrazide.*—0.4 gram of phenylhydrazine was dissolved in 1 gram of heptoic acid. After forty hours a considerable quantity of the hydrazide had crystallized out. After six days water was added and 0.69 gram obtained (86.4 per cent. of the theory). The product is nearly insoluble in cold water, difficultly soluble in cold, easily in hot alcohol, from which it crystallizes in thin transparent prisms melting at 103°–104°.

0.1440 gram of substance gave 0.3754 gram of carbon dioxide and 0.1178 gram of water.

| | Calculated for $C_6H_5N_2H_2COC_6H_{13}$. | Found. |
|---|---|---|
| C | 70.91 | 71.08 |
| H | 9.09 | 9.16 |

### *Action of Phenylhydrazine upon Acetylenedicarboxylic Acid.*

As has been shown[1] phenylhydrazine hydrochloride acts upon acetylenedicarboxylic acid in aqueous solution to form 1-phenyl-5-pyrazolon-3-carboxylic acid. The following experiments show that in the presence of acetic acid, or if an excess of the acid itself is used, the same compound is formed; but if an excess of phenylhydrazine is used, a different compound results.

To 0.5 gram of acetylenedicarboxylic acid, dissolved in 2 grams of glacial acetic acid, was added 0.5 gram of phenylhydrazine in 3 grams of glacial acetic acid. After standing three days 0.87 gram of crystallized substance was obtained which, washed with water and crystallized from alcohol, began to turn brown at 240° and decomposed at 265°–266°, (characteristic of 1-phenyl-5-pyrazolon-3-carboxylic acid).[2] With a solution of ferric chloride it gave a deep violet color.

To 0.2 gram of acetylenedicarboxylic acid, dissolved in 4 cc. of water, 0.2 gram of phenylhydrazine was added. Crystals began to separate after about two hours. After twenty-four hours 0.28 gram was obtained, which, crystallized from alcohol, decomposed at 265°–266°.

An experiment made in aqueous solution with an excess of phenylhydrazine gave a crystalline product possessing none of the properties of 1-phenyl-5-pyrazalon-3-carboxylic acid. Its composition has not yet been determined.

TUFTS COLLEGE, May, 1898.

[1] Michael and Bucher, communicated by the authors.

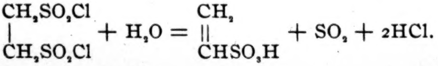
[2] Michael and Bucher.

# ALIPHATIC SULPHONIC ACIDS.

## II. ETHYLENESULPHONIC ACIDS.

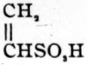
BY ELMER P. KOHLER.

In a previous paper[1] I showed that unsaturated sulphonic acids can be prepared by decomposing the chlorides of saturated polysulphonic acids with water. The method was illustrated with (1,2)-ethanedisulphone chloride, which reacts with boiling water to form ethylenesulphonic acid :



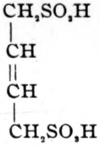
$$\begin{array}{l} CH_2SO_2Cl \\ | \\ CH_2SO_2Cl \end{array} + H_2O = \begin{array}{l} CH_2 \\ \| \\ CHSO_3H \end{array} + SO_2 + 2HCl.$$

That the product of this reaction is the lowest member of the unsaturated sulphonic acid series (I), and not an isomeric disulphonic acid (II),



$$\begin{array}{l} CH_2 \\ \| \\ CHSO_3H \end{array}$$

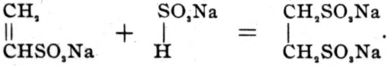
I.



$$\begin{array}{l} CH_2SO_3H \\ | \\ CH \\ \| \\ CH \\ | \\ CH_2SO_3H \end{array}$$

II.

was shown by the fact that the salts of the acid combine with acid sulphites to form the corresponding salts of (1,2)-ethanedisulphonic acid :



$$\begin{array}{l} CH_2 \\ \| \\ CHSO_3Na \end{array} + \begin{array}{l} SO_3Na \\ | \\ H \end{array} = \begin{array}{l} CH_2SO_3Na \\ | \\ CH_2SO_3Na \end{array}.$$

In confirmation of this view, it has since been found that the acid can be reduced to ethanesulphonic acid, and that it combines with water and the halogen acids to form derivatives of ethanesulphonic acid.

### *Methods of Preparation.*

1. *From (1,2)-Ethanedisulphone Chloride.*—A suitable quantity of (1,2).ethanedisulphone chloride is placed in a flask

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[1] This Journal, 19, 730.

with about five times its weight of water, the flask connected with an inverted condenser, and the whole boiled until all the chloride has disappeared. The resulting liquid is then transferred to an evaporating dish and concentrated on a steam-bath until a few drops of the residue no longer give a precipitate with silver nitrate solution. The amber-colored liquid still contains some (1,2)-ethanedisulphonic acid mixed with the ethylenesulphonic acid. If the liquid is allowed to stand for a few days most of the disulphonic acid separates out in the form of long colorless needles, which can be removed by filtration. A still further separation can be obtained by mixing the filtrate with its own volume of glacial acetic acid, and again allowing it to stand for a few days. To get pure ethylenesulphonic acid, however, it is necessary to make use of the salts. All the salts of (1,2)-ethanedisulphonic acid are insoluble in 95 per cent. alcohol, while the potassium, sodium, and ammonium salts of ethylenesulphonic acid are readily soluble in alcohol of this strength. To get the free acid it is best to use the ammonium salt. The amber-colored liquid is diluted to twice its volume, neutralized with solid ammonium carbonate, and evaporated to dryness. To remove the last traces of water, without decomposing the unsaturated sulphonic acid, it is necessary to add small quantities of absolute alcohol and repeat the evaporation. The fine, yellowish powder thus obtained is then transferred to a flask connected with an inverted condenser, and boiled with absolute alcohol. From the alcoholic solution the ammonium salt of the unsaturated acid crystallizes, on cooling, in perfectly pure condition.

To pass back to the acid, the ammonium salt is changed into the lead salt by boiling the aqueous solution with pure lead carbonate, the lead removed by precipitation as sulphide, and the resulting solution evaporated on the water-bath, and over sulphuric acid. The acid obtained in this way is an oily liquid without any tendency toward crystallization. It can stand over phosphorus pentoxide for months without change, and glacial acetic acid—the best solvent for aliphatic sulphonic acids—deposits it as an oil. The analyses show that it is pure ethylenesulphonic acid.

I. 0.3280 gram substance gave 0.2660 gram $CO_2$ and 0.1095 gram $H_2O$.

II. 0.4162 gram substance gave 0.3365 gram $CO_2$ and 0.1392 gram $H_2O$.

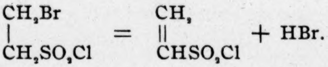
III. 0.2515 gram substance gave 0.5435 gram $BaSO_4$.

IV. 0.2050 gram substance gave 0.4430 gram $BaSO_4$.

|  | Calculated for $C_2H_4SO_3$. | Found. |  |  |  |
|---|---|---|---|---|---|
|  |  | I. | II. | III. | IV. |
| C | 22.2 | 22.1 | 21.9 | .... | .... |
| H | 3.7 | 3.9 | 3.8 | .... | .... |
| S | 29.6 | .... | .... | 29.71 | 29.8 |

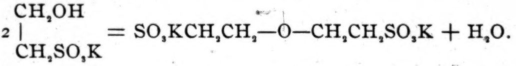
The acid mixes, in all proportions, with water, alcohol, and glacial acetic acid. It is difficultly soluble in ether and chloroform.

2. *From (1,2)-Bromethanesulphone Chloride.*—When (1,2)-bromethanesulphone chloride is distilled under atmospheric pressure it undergoes slight decomposition accompanied by evolution of hydrobromic acid. The distillate reacts with bromine, indicating the presence of an unsaturated compound. By distilling under increased pressure the amount of decomposition can be considerably increased. 50 grams of the sulphone chloride were slowly distilled under an increased pressure of about 1 meter of mercury, and the process repeated with the distillate until no further evolution of hydrobromic acid was observed. The resulting liquid was a mixture of sulphone chlorides which could not be separated by fractional distillation under any pressure. It was, therefore, decomposed by boiling with water, the hydrochloric acid precipitated as lead chloride, the lead removed as sulphide, and the acid neutralized with potassium carbonate. The mixture of salts obtained by evaporating this liquid to dryness was separated by recrystallization from alcohol and found to contain about equal amounts of (1,2)-bromethanesulphonate and ethylenesulphonate. From 50 grams of chloride 8.6 grams of potassium ethylenesulphonate were obtained. The solution obtained by neutralizing the mixed chlorides contained no hydrobromic acid, hence the unsaturated acid must have been formed during distillation.



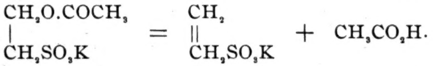
$$\begin{array}{l}CH_2Br\\ |\\ CH_2SO_2Cl\end{array} = \begin{array}{l}CH_2\\ \|\\ CHSO_2Cl\end{array} + HBr.$$

3. *From Isethionic Acid.*—As is well known, isethionates, when heated to 200°, lose water and pass almost quantitatively into di-isethionates:



$$2\begin{array}{l}CH_2OH\\ |\\ CH_2SO_3K\end{array} = SO_3KCH_2CH_2—O—CH_2CH_2SO_3K + H_2O.$$

At a higher temperature the di-isethionates are decomposed, the sulphuric acid group being split off as sulphite. If, however, the isethionates are first changed into the acetic acid esters and then heated, acetic acid is split off, and the corresponding salts of ethylenesulphonic acid are formed. 40 grams of potassium isethionate were boiled with acetyl chloride until no further elimination of hydrochloric acid took place. The liquid was evaporated to dryness and the product crystallized from absolute alcohol. The salt, heated in a shallow vessel in an oil-bath began to soften at 160°. At 170° the odor of acetic acid became perceptible, while at 185° the salt began to froth, and soon solidified to a dark, glassy mass. This was dissolved in 95 per cent. alcohol, the solution decolorized with bone-black, and evaporated to crystallization. 18.8 grams of pure potassium ethylenesulphonate were obtained.



$$\begin{array}{l}CH_2O.COCH_3\\ |\\ CH_2SO_3K\end{array} = \begin{array}{l}CH_2\\ \|\\ CH_2SO_3K\end{array} + CH_3CO_2H.$$

The method works equally well with sodium, potassium, and barium isethionates, but does not give good results with ammonium isethionate. The reaction promises to be particularly valuable for the preparation of more complex unsaturated sulphonic acids.

### *Salts of Ethylenesulphonic Acid.*

*The ammonium salt* is readily obtained in perfectly pure condition, by neutralizing the acid with ammonium carbonate, evaporating to dryness, and crystallizing the residue from absolute alcohol.

I. 0.4165 gram salt gave 37.1 cc. N, at 27° and under a pressure of 748 mm.

II. 0.3212 gram salt gave 30.2 cc. N, at 28° and under a pressure of 744 mm.

| | Calculated for $C_2H_7NSO_3$. | Found. I. | II. |
|---|---|---|---|
| N | 11.2 | 11.2 | 11.4 |

The salt is extremely soluble in water, moderately soluble in cold aqueous, and boiling absolute alcohol; insoluble in ether. If its solution in aqueous alcohol is allowed to evaporate spontaneously, it separates in large orthorhombic tables. From a solution in boiling absolute alcohol it separates, on cooling, in short needles or prisms. Especially characteristic is its behavior on heating. If a small quantity is heated rapidly in a capillary tube, it melts completely at 156°, but it immediately solidifies again and, if heated higher, begins to decompose a few degrees above this point. If a larger quantity of the salt is kept at 156°, it remains liquid for some time but ultimately solidifies to a horny mass, which is no longer soluble in alcohol. It was impossible to determine the nature of the change which takes place at this temperature, as no pure product could be isolated. If the temperature is kept sufficiently low there is no loss in weight; the product is colorless, reacts with bromine and permanganate in the cold, and gives off ammonia with alkalies.

*The potassium salt* was prepared by neutralizing the acid with potassium carbonate, evaporating to dryness, and crystallizing the residue from 95 per cent. alcohol.

I. 0.2125 gram of the air-dried salt gave 0.1271 gram $K_2SO_4$.

II. 0.1955 gram of the salt gave 0.1170 gram $K_2SO_4$.

| | Calculated for $C_2H_3SO_3K$. | Found. I. | II. |
|---|---|---|---|
| K | 26.71 | 26.75 | 26.88 |

The salt is very soluble in water, moderately soluble in boiling 95 per cent. alcohol, insoluble in absolute alcohol. From water it crystallizes in large plates, from alcohol in thin spear-shaped needles. It deliquesces in moist air.

*The sodium salt* was prepared like the potassium salt, which it resembles in crystal form and properties.

I. 0.2323 gram salt gave 0.1275 gram $Na_2SO_4$.

II. 0.2217 gram salt gave 0.1220 gram $Na_2SO_4$.

| | Calculated for $C_2H_3SO_3Na$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| Na | 17.69 | 17.77 | 17.85 |

*The barium salt* was prepared by neutralizing the acid with barium carbonate and evaporating to crystallization. The salt is insoluble in alcohol. From water it crystallizes in minute needles, containing 1 molecule of water of crystallization, which is given off below 110°.

I. 0.4520 gram of the salt lost 0.0225 gram $H_2O$.

II. 0.3298 gram of the salt lost 0.0162 gram $H_2O$.

| | Calculated for $(C_2H_3SO_3)_2Ba.H_2O$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| $H_2O$ | 4.87 | 4.98 | 4.91 |

I. 0.2100 gram of the anhydrous salt gave 0.1394 gram $BaSO_4$.

II. 0.2567 gram of the anhydrous salt gave 0.1710 gram $BaSO_4$.

| | Calculated for $(C_2H_3SO_3)_2Ba$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| Ba | 39.1 | 39.1 | 39.22 |

*The lead salt* was obtained by neutralizing the acid with lead carbonate and recrystallizing from cold water. It crystallizes in hard, lustrous prisms, which are difficultly soluble in cold water. It is impossible to drive off all the water of crystallization without decomposing the salt. The analyses of the hydrous salt lead to the formula $(C_2H_3SO_3)_2Pb.2H_2O$.

I. 0.3215 gram substance gave 0.2750 gram $PbSO_4$.

II. 0.1621 gram substance gave 0.1376 gram $PbSO_4$.

| | Calculated for $(C_2H_3SO_3)_2Pb.2H_2O$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| Pb | 57.96 | 58.27 | 57.9 |

*Ethylenesulphone chloride* was prepared by treating the potassium salt, suspended in chloroform, with slightly more than the calculated quantity of phosphorus pentachloride. After the reaction, which takes place in the cold, was complete, the potassium chloride formed was removed by filtration, and the chloroform by distillation. As it was found that the chlorides of phosphorus could not be completely removed by distillation, the residue was poured into ice-water and washed until free from phosphorus. It was then dissolved in ether, the ethereal solution dried by means of calcium chloride and, finally, purified by fractional distillation under diminished pressure.

The chloride is an oily liquid which cannot be distilled under atmospheric pressure. Under a pressure of 250 mm. it boils at 118°–120° with slight decomposition.

I. 0.2621 gram substance gave 0.2640 gram AgCl.

II. 0.2428 gram substance gave 0.2450 gram AgCl.

|  | Calculated for | Found. |  |
|---|---|---|---|
|  | $C_2H_3ClSO_2$. | I. | II. |
| Cl | 24.91 | 24.9 | 25.0 |

When decomposed with boiling water the chloride gives ethylenesulphonic acid.

## TRANSFORMATIONS OF ETHYLENESULPHONIC ACID.

### *Oxidation.*

The acid is oxidized with the greatest ease. It reduces acid, neutral, and alkaline permanganate solutions in the cold. In acid solution the reaction with permanganate is quantitative :

0.1120 gram of the potassium salt, dissolved in water and acidified with sulphuric acid, decolorized 46.3 cc. of a normal potassium permanganate solution (1 cc. = 0.016 gram oxygen, in acid solution), corresponding to 95.8 grams oxygen per molecular weight of salt.

0.2009 gram of the same salt decolorized 92.7 cc. of the permanganate solution, corresponding to 95.9 grams oxygen per molecular weight of salt.

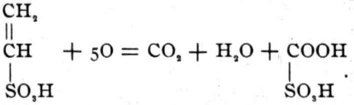
The oxidation, therefore, takes place according to the equation :

$$C_2H_3SO_3H + 6O = 2CO_2 + H_2O + H_2SO_4.$$

In acid and neutral solutions the reaction is instantaneous. In very strongly alkaline solutions it takes place more slowly, but the products are the same. Sulphuric acid can be detected in the liquid after a small quantity of permanganate has been added; and, if the amount of permanganate added is insufficient for complete oxidation according to the equation given, a corresponding amount of substance can be recovered unchanged.

The ease with which the substance is oxidized is best seen in its behavior towards silver nitrate solution. If a quantity of the potassium salt is added to an ammoniacal solution of silver nitrate, and the liquid warmed until deposition of silver just begins, the reaction continues even after cooling, until all the salt is oxidized or all the silver deposited.

Many other methods of oxidation were tried in the hope of getting sulphoformic acid according to the equation:



$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ SO_3H \end{array} + 5O = CO_2 + H_2O + \begin{array}{l} COOH \\ | \\ SO_3H \end{array}.$$

The result, however, was the same in all cases. All oxidizing agents which attack ethylenesulphonic acid destroy it completely, forming sulphuric acid, carbon dioxide, and water.

### *Reduction.*

The acid is reduced with difficulty. Sodium amalgam, which reduces acrylic acid to propionic acid, seems to have no effect upon the analogous sulphonic acid. 50 cc. of a solution of the sodium salt, of such a strength that 1 cc. was capable of reducing 10 cc. of standard permanganate, was kept in contact with sodium amalgam for six days, then acidified and brought to known volume, when 1 cc. was found equivalent to 9.6 cc. of the permanganate solution. There was no reduction. 50 cc. of the same solution were then warmed with the sodium amalgam for five hours, when it was found that the solution no longer reduced permanganate. On concentrating the alkaline liquid a sodium salt crystallized out. This was purified by recrystallizing it from alcohol.

I. 0.3543 gram substance gave 0.2090 gram $CO_2$, and 0.1081 gram $H_2O$.

II. 0.2998 gram substance gave 0.1769 gram $CO_2$, and 0.0910 gram $H_2O$.

III. 0.1895 gram substance gave 0.0910 gram $Na_2SO_4$.

IV. 0.2110 gram substance gave 0.1015 gram $Na_2SO_4$.

|  | Calculated for $C_2H_5SO_4Na$. | Found. |  |  |  |
|---|---|---|---|---|---|
|  |  | I. | II. | III. | IV. |
| C | 16.2 | 16.1 | 16.2 | .... | .... |
| H | 3.4 | 3.3 | 3.4 | .... | .... |
| Na | 15.54 | .... | .... | 15.55 | 15.79 |

The substance is not a reduction-product of ethylenesulphonic acid; but a salt of oxyethanesulphonic acid formed by the addition of water to the unsaturated acid:

$$C_2H_3SO_3Na + H_2O = C_2H_4OHSO_3Na.$$

The filtrate from this salt was neutralized with sulphuric acid, concentrated and freed from most of the sodium sulphate by addition of alcohol. The filtrate from the sodium sulphate was evaporated to dryness, and extracted with alcohol. No other organic salt was present.

Attempts to reduce the acid with nascent hydrogen in acid solution met with no better success. A solution of the acid, of known reducing power, was boiled with zinc and dilute sulphuric acid for twenty hours without any appreciable change.

Ten gram portions of the acid were finally sealed up with hydriodic acid and phosphorus and heated to 170° for ten hours. After the iodine and hydriodic acid had been removed, in the usual way, the liquid was neutralized with potassium carbonate, evaporated to small volume and poured into alcohol. A potassium salt separated out and was purified by recrystallization from water.

I. 0.4365 gram substance gave 0.2580 gram $CO_2$, and 0.1335 gram $H_2O$.

II. 0.3576 gram substance gave 0.2100 gram $CO_2$, and 0.1124 gram $H_2O$.

III. 0.2108 gram substance gave 0.1245 gram $K_2SO_4$.

IV. 0.1898 gram substance gave 0.1116 gram $K_2SO_4$.

|  | Calculated for $C_2H_5SO_3K$. | Found. |  |  |  |
|---|---|---|---|---|---|
|  |  | I. | II. | III. | IV. |
| C | 16.2 | 16.1 | 16.0 | .... | .... |
| H | 3.4 | 3.4 | 3.6 | .... | .... |
| K | 26.35 | .... | .... | 26.49 | 26.36 |

The salt has the composition and properties of potassium ethanesulphonate. For further identification it was treated with phosphorus pentachloride. The product, after purification, boiled at 171°—the boiling-point of the ethanesulphone chloride.

On concentrating the alcoholic solution a second salt was obtained. This, as shown by the analyses, was potassium oxyethanesulphonate:

I. 0.3015 gram substance gave 0.1598 gram $CO_2$, and 0.0825 gram $H_2O$.

II. 0.4522 gram substance gave 0.2410 gram $CO_2$, and 0.1507 gram $H_2O$.

III. 0.1521 gram substance gave 0.0802 gram $K_2SO_4$.

IV. 0.1155 gram substance gave 0.0612 gram $K_2SO_4$.

| | Calculated for $C_2H_5SO_4K$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| C | 14.6 | 14.4 | 14.3 | .... | .... |
| H | 3.04 | 3.4 | 3.0 | .... | .... |
| K | 23.7 | .... | .... | 23.6 | 23.7 |

These results show that when ethylenesulphonic acid is heated with hydriodic acid and phosphorus two reactions take place:

$$\text{I. } C_2H_3SO_3H + 2H = C_2H_5SO_3H.$$

$$\text{II. } C_2H_3SO_3H + H_2O = C_2H_4OHSO_3H.$$

## *Addition of Water.*

Aqueous solutions of ethylenesulphonic acid are quite stable at the boiling-point of water. Moderately concentrated solutions of the acid and of the potassium salt were boiled for ten hours without diminution in reducing power. The same solutions were then sealed up and heated to 150°. After heating for ten hours, the solutions no longer reduced permanganate in the cold. The acid was neutralized with potassium carbonate, the two solutions were evaporated to dryness, and the residues recrystallized from alcohol. The product in both cases was the potassium oxyethanesulphonate, which was obtained when the acid was heated with hydriodic acid.

In crystal form and solubility, the salt agrees closely with Liebig's description of potassium isethionate. Liebig states that potassium isethionate melts at 350° and does not lose water below this point. The potassium salt obtained by me melts sharply at 190° and loses water below 200°, passing into the anhydride, $C_4H_8S_2O_7K_2$.

I. 0.2240 gram salt gave 0.1265 gram $K_2SO_4$.

II. 0.2042 gram salt gave 0.1146 gram $K_2SO_4$.

| | Calculated for $C_4H_8S_2O_7K_2$. | Found. I. | II. |
|---|---|---|---|
| K | 25.2 | 25.3 | 25.2 |

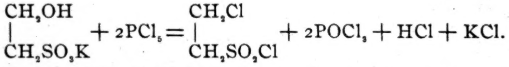
When treated with phosphorus pentachloride the salt gave a chloride boiling at 200°, the boiling-point of (1,2)-chlorethanesulphone chloride.

I. 0.2167 gram substance gave 0.3828 gram AgCl.

II. 0.1850 gram substance gave 0.3255 gram AgCl.

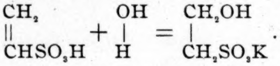
| | Calculated for $C_2H_4SO_2Cl_2$. | Found. I. | II. |
|---|---|---|---|
| Cl | 43.6 | 43.8 | 43.6 |

This could only have been formed from a (1,2)-oxyethanesulphonic acid :



$$\begin{array}{l}CH_2OH\\ |\\ CH_2SO_3K\end{array} + 2PCl_5 = \begin{array}{l}CH_2Cl\\ |\\ CH_2SO_2Cl\end{array} + 2POCl_3 + HCl + KCl.$$

Hence, when ethylenesulphonic acid combines with water the hydroxyl group goes into the (2)-position with reference to the sulphoxyl group :

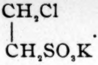


$$\begin{array}{l}CH_2\\ \|\\ CHSO_3H\end{array} + \begin{array}{c}OH\\ |\\ H\end{array} = \begin{array}{l}CH_2OH\\ |\\ CH_2SO_3K\end{array}.$$

Since but one (1,2)-oxyethanesulphonic acid is theoretically possible, the experiments of Liebig were repeated. The potassium isethionate obtained melted at 190° and decomposed below 200°. The high temperatures observed by Liebig and Berzelius must have been due to some impurity introduced with the alcohol with which they started.

These experiments show that water can be added to ethylenesulphonic acid and its salts without the presence of other substances. The addition takes place much more readily in alkaline solution. If an alkaline solution of the potassium salt is boiled for a few hours, the salt is completely transformed into isethionate, and if a small quantity of alcoholic potash is added to an alcoholic solution of the same salt, the transformation takes place in the cold.

## *Addition of Hydrochloric Acid.*

A quantity of the potassium salt was heated with concentrated hydrochloric acid for five hours at 130°. The resulting liquid was diluted until the potassium chloride that had separated was redissolved, then neutralized with lead carbonate and the filtrate from the lead chloride evaporated to dryness. The residue contained two salts which were separated by fractional crystallization from alcohol. About 75 per cent. of the product was the potassium salt of (1,2)-chlorethanesulphonic acid,  $\begin{array}{l} CH_2Cl \\ | \\ CH_2SO_3K \end{array}$.

I. 0.1878 gram substance gave 0.1469 gram AgCl.
II. 0.1993 gram substance gave 0.1574 gram AgCl.
III. 0.1629 gram substance gave 0.0771 gram $K_2SO_4$.
IV. 0.1941 gram substance gave 0.0930 gram $K_2SO_4$.

| | Calculated for $C_2H_4ClSO_3K$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Cl | 19.45 | 19.36 | 19.55 | .... | .... |
| K | 21.36 | .... | .... | 21.21 | 21.46 |

The position of the chlorine atom was determined by treating the salt with phosphorus pentachloride, when (1,2)-chlorethane chloride, boiling at 200°, was obtained.

The second product was potassium isethionate, formed by the addition of water.

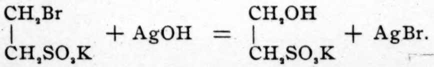
### *Addition of Hydrobromic Acid.*

The addition of hydrobromic acid takes place under the same conditions as that of hydrochloric acid. The product is the potassium salt of (1,2)-bromethanesulphonic acid.

I. 0.2127 gram substance gave 0.1760 gram AgBr.
II. 0.2427 gram substance gave 0.2019 gram AgBr.
III. 0.1828 gram substance gave 0.0710 gram $K_2SO_4$.
IV. 0.3122 gram substance gave 0.1199 gram $K_2SO_4$.

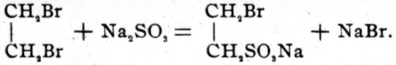
| | Calculated for $C_2H_4BrSO_3K$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Br | 35.24 | 35.25 | 35.47 | .... | .... |
| K | 17.18 | .... | .... | 17.4 | 17.22 |

The salt is readily soluble in water and alcohol. From water it crystallizes in orthorhombic tables, from absolute alcohol in thin, friable laminæ. To determine the position of the bromine atom the salt was boiled with silver oxide until all the bromine was replaced with hydroxyl. The product was potassium isethionate.



$$\begin{array}{l} CH_2Br \\ | \\ CH_2SO_3K \end{array} + AgOH = \begin{array}{l} CH_2OH \\ | \\ CH_2SO_3K \end{array} + AgBr.$$

The sodium salt of the same bromethanesulphonic acid was obtained, in quantity, by slowly adding sodium sulphite to a boiling solution of ethylene bromide in water to which a small quantity of alcohol had been added. If the ethylene bromide is kept in excess, only one of its bromine atoms is replaced :



$$\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} + Na_2SO_3 = \begin{matrix}CH_2Br\\ |\\ CH_2SO_3Na\end{matrix} + NaBr.$$

The results of a detailed study of the acid will be published in a separate paper.

### *Reaction between Ethylenesulphonic Acid and Bromine.*

Aqueous solutions of ethylenesulphonic acid rapidly decolorize bromine water in the cold. The result, however, is not addition but substitution. Hydrobromic acid can be detected in the liquid after a single drop of bromine has been added and, as the following results show, a molecule of hydrobromic acid is formed for every molecule of bromine that enters into reaction.

In the following experiments definite quantities of bromine were added to dilute solutions of the acid contained in measuring-flasks. After shaking until the color of bromine had disappeared, the solutions were brought to known volume and the hydrobromic acid determined volumetrically. As the bromine was drawn from burettes, and, as the last portions react very slowly, the results are not quite accurate. The calculations are based on the equation :

$$C_2H_3SO_3H + Br_2 = C_2H_2BrSO_3H + HBr.$$

I. 1.549 grams bromine, added to an excess of the acid, liberated 0.7802 gram hydrobromic acid instead of 0.7841 gram calculated.

II. 2.425 grams bromine added to an excess of the potassium salt, liberated 1.250 grams hydrobromic acid instead of 1.228 grams calculated.

III. 2.0634 grams of the potassium salt reacted with 2.3592 grams bromine instead of 2.2606 grams calculated.

These results show that the above equation accurately expresses the course of the reaction. To isolate the organic product of the reaction the hydrobromic acid was precipitated as lead bromide, the lead removed as sulphide, the acid thus obtained neutralized with potassium carbonate, and the solution evaporated to dryness. The residue was almost completely soluble in boiling absolute alcohol. On cooling the alcoholic solution a potassium salt separated in long colorless needles. The salt was washed with ether, dried at 50°, and analyzed.

I. 0.5135 gram substance gave 0.2051 gram $CO_2$, and 0.0411 gram $H_2O$.

II. 0.5288 gram substance gave 0.2075 gram $CO_2$, and 0.0431 gram $H_2O$.

III. 0.1907 gram substance gave 0.1598 gram AgBr.

IV. 0.1832 gram substance gave 0.1530 gram AgBr.

V. 0.2108 gram substance gave 0.2192 gram $BaSO_4$.

VI. 0.2122 gram substance gave 0.2190 gram $BaSO_4$.

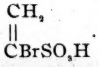
VII. 0.1728 gram substance gave 0.0663 gram $K_2SO_4$.

VIII. 0.2601 gram substance gave 0.0998 gram $K_2SO_4$.

|  | Calculated for $C_2H_2BrSO_3K$. | Found. |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
| C | 10.66 | 10.86 | 10.72 | .... | .... | .... | .... | .... | .... |
| H | 0.88 | 0.93 | 0.98 | .... | .... | .... | .... | .... | .... |
| Br | 35.55 | .... | .... | 35.72 | 35.6 | .... | .... | .... | .... |
| S | 14.22 | .... | .... | .... | .... | 14.31 | 14.15 | .... | .... |
| K | 17.33 | .... | .... | .... | .... | .... | .... | 17.15 | 17.19 |

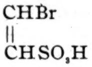
The salt cannot be crystallized from water. It is readily soluble in aqueous alcohol, moderately soluble in boiling, absolute alcohol. It is extremely hygroscopic, deliquescing rapidly in the air.

The structure of this substance is not yet determined with absolute certainty; but its properties are most easily explained on the assumption that it is a salt of (1)-bromethylenesulphonic acid,



$$\begin{array}{l} CH_2 \\ \| \\ CBrSO_3H \end{array}.$$

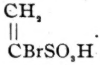
If a solution of the acid, or any of its salts, is shaken with a dilute solution of barium hydroxide, it is rapidly destroyed, the sulphonic acid residue being split off and precipitated as barium sulphite while the bromine remains in solution as bromide. From the solution ether extracts a substance which on evaporation separates out as a gum insoluble in ether and alcohol, soluble in water. Every effort to obtain the substance in a form fit for analysis failed. In the air it hardens into a horny mass of variable composition. Silver oxide and cold permanganate have no action upon it, while hot acid permanganate oxidizes it to carbon dioxide and water. Nitric acid gives a small quantity of oxalic acid. The structure of a monobromethylenesulphonic acid must be either



$$\begin{array}{l}\mathrm{CHBr}\\ \| \\ \mathrm{CHSO_3H}\end{array}$$

I.

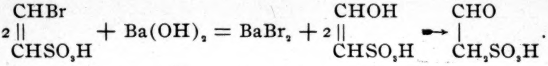
or



$$\begin{array}{l}\mathrm{CH_2}\\ \| \\ \mathrm{CBrSO_3H}\end{array}.$$

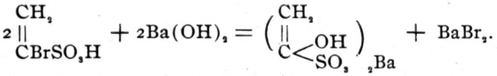
II.

Since, on treatment with barium hydroxide, the bromine goes into solution as bromide, the primary action of the hydroxide is probably the replacement of bromine by hydroxyl. This, in the case of a substance with the formula I., ought to give a fairly stable sulphonic acid :



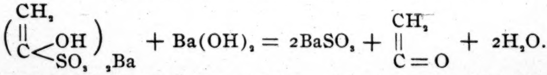
$$2\begin{array}{l}\mathrm{CHBr}\\ \| \\ \mathrm{CHSO_3H}\end{array} + \mathrm{Ba(OH)_2} = \mathrm{BaBr_2} + 2\begin{array}{l}\mathrm{CHOH}\\ \| \\ \mathrm{CHSO_3H}\end{array} \longrightarrow \begin{array}{l}\mathrm{CHO}\\ | \\ \mathrm{CH_2SO_3H}\end{array}.$$

The same change in a substance with the structure represented by II., would give an arrangement that is known to be unstable :

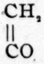


$$2\begin{array}{l}\mathrm{CH_2}\\ \| \\ \mathrm{CBrSO_3H}\end{array} + 2\mathrm{Ba(OH)_2} = \left(\begin{array}{l}\mathrm{CH_2}\\ \| \\ \mathrm{C}{<}\begin{array}{l}\mathrm{OH}\\ \mathrm{SO_3}\end{array}\end{array}\right)_2\mathrm{Ba} + \mathrm{BaBr_2}.$$

All (1,1)-oxysulphonic acids are readily decomposed by alkalies, the sulphonic acid group being split off as sulphite. With barium hydroxide a sulphonic acid, like the above, would be expected to react according to the equation :



$$\left(\begin{array}{l}\mathrm{CH_2}\\ \| \\ \mathrm{C}{<}\begin{array}{l}\mathrm{OH}\\ \mathrm{SO_3}\end{array}\end{array}\right)_2\mathrm{Ba} + \mathrm{Ba(OH)_2} = 2\mathrm{BaSO_3} + \begin{array}{l}\mathrm{CH_2}\\ \| \\ \mathrm{C=O}\end{array} + 2\mathrm{H_2O}.$$

Formula II., therefore, explains the ease with which the sulphonic acid group is split off and also the formation of the gum obtained, as a substance with the structure  $\begin{array}{l}\mathrm{CH_2}\\ \| \\ \mathrm{CO}\end{array}$ would probably polymerize as fast as formed.

## *Summary.*

The properties of ethylenesulphonic acid are, in the main, such as would be expected in a ($\Delta$-1,2) unsaturated sulphonic acid. From the corresponding saturated acid it differs markedly, in its sensitiveness to reagents: it is easily oxidized, it combines with a number of substances, and it readily exchanges a part of its hydrogen for halogens and for acid groups.

Like most of the unsaturated carbonic acids, ethylene sulphonic acid instantly reduces a solution of permanganate. In its behavior towards oxidizing agents it differs from unsaturated carbonic acids, in that no intermediate oxidation-products are formed. All oxidizing agents, which attack the acid, completely destroy it, forming carbon dioxide, water, and sulphuric acid.

The acid is reduced with difficulty, sodium amalgam in alkaline solution, and zinc in acid solution, have no effect on it. When heated with hydriodic acid, however, it is reduced to ethanesulphonic acid.

Ethylenesulphonic acid readily combines with water and the halogen acids. In all cases the combination takes place in the same way as with ($\Delta$-1,2) unsaturated carbonic acids—the negative component of the molecule added does not unite with the carbon atom which has the smallest number of hydrogen atoms in combination with it, but always goes into the (2)-position with reference to the sulphoxyl group.

The behavior of the acid towards bromine is peculiar. While the two react at all temperatures above the freezing-point of water, and in all solvents, the result is not addition but substitution. The product is (1,1-)bromethylenesulphonic acid. A similar result has been obtained with a few unsaturated carbonic acids. In these cases it is generally assumed that the first reaction is addition of bromine, and that this is followed by rearrangement and subsequent splitting off of hydrobromic acid. Such an assumption is not permissible in the present case because the dibromethanesulphonic acid, which would be formed by the addition of bromine to ethylenesulphonic acid can be prepared in a different way and is perfectly stable up to the boiling-point of water.

Chemical Laboratory, Bryn Mawr College.

# NOTES.

## *Krypton, Neon, Metargon, and Coronium—Recently Discovered Constituents of the Atmosphere.*

The discovery of rubidium and caesium by Bunsen and Kirchhoff by the use of the spectroscope opened up a new field for investigation and a study by this method of the solid constituents of the earth revealed several hitherto unknown elements. A more recent investigation, in the same general lines, of the gaseous envelope of the earth, all of whose constituents were supposed to have been isolated and identified, has led to equally surprising results. In the course of the study of argon and helium and attempts to purify them, three new gases have been isolated. An investigation carried on by Ramsay and others showed that no new gases could be obtained from the nitride of magnesium, formed in the preparation of argon; but a study of the residue from liquid air gave unexpected results. In a communication to the Royal Society,[1] Prof. Ramsay and Mr. Travers gave a preliminary notice of the isolation of a new gas. By allowing 750 cc. of liquid air to evaporate until only 10 cc. were left, collecting the gas from this and, after removing the oxygen and nitrogen, sparking over caustic soda with oxygen, they obtained 26.2 cc. of a gas which showed two spectra, a feeble argon spectrum and one which had not before been observed. This latter is characterized by the presence of two very brilliant lines, one almost identical with $D_3$ and another, a green line, comparable with the green helium line. Measurements by Mr. Baly show the presence of the following lines, all four of which are in the field at the same time:

$D_1$ 5895.0, $D_2$ 5889.0, $D_3$ 5875.9, $D_4$ 5867.7.

The spectrum of this gas and that of argon were compared and the results were such as to characterize the gas as one before unknown. The density of the gas, taking the average of two determinations, was 22.49 if oxygen is taken as 16. The determination of the velocity of sound in the gas showed it to be, like argon and helium, monatomic, and of an elementary character. To this constituent of the atmosphere, which is heavier than argon and less volatile than nitrogen, oxygen and argon, they have given the name "krypton" (hidden).

In a later communication[2] to the Royal Society the same authors announce the discovery of two more constituents of atmospheric air. Dr. Norman Collie succeeded, by long-continued diffusion, in separating argon into two portions, one with a density of 19.93 and the other with that of 20.21, a difference too slight to admit of any conclusion as to the presence of more than one substance.

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[1] Proc. Royal Soc., 63, 405.

[2] *Ibid.*, 63, 437.

By the liquefaction of large volumes of argon, using liquid air as the cooling agent, Ramsay and Travers have isolated two gases which they consider to be hitherto unknown elements. When argon was allowed to enter a bulb, cooled by liquid air, it formed a liquid; but at the same time a white solid appeared on the sides and in the liquid. After standing some time this mixture was allowed to evaporate slowly and fractions were taken off from time to time. The liquid evaporated off first and practically all of it could be removed before there was any marked change in the solid. The latter evaporated slowly, the last portion when the bulb was removed from the protecting jacket and the finger applied to the surface of the glass. The lighter gas which first evaporated had a density of 17.2, which decreased after further purification to 14.67 and, after a preliminary fractionation, to 13.7. In order to occupy the place in the periodic system which it would be expected to fill, it should have a density of 10 or 11, and the fact that the partial purification reduced the density from 17.2 to 13.7 gives hope of further reduction. An examination of the gas, after it had been sparked with oxygen, showed the presence of a number of bright red lines, a bright yellow one, and less conspicuous green and blue lines. The yellow line, although equal in intensity to the yellow lines of sodium, helium, and krypton, was found to have a different wave-length from any of these. This gas, to which they give the name "neon" (new), behaves in a vacuum-tube entirely differently from other known gases. It is rapidly absorbed by the red hot aluminium electrodes, and the color changes from a carmine-red to a brilliant orange.

The gas obtained from the white solid, after the liquid had boiled away, gave a spectrum which was entirely different from that of argon, although resembling it in general character. With low dispersion it gave a banded spectrum; but with a grating single, equidistant, bright lines appeared with the intermediate spaces filled with dim lines. The density of the gas is practically identical with that of argon, being 19.87, and it is monatomic. As the gas had a different spectrum from argon, and behaved differently ~~at~~ low temperatures, they concluded that it was elementary and called it "metargon." It holds the same position towards argon that nickel does to cobalt, having approximately the same atomic weight but different properties. They believed the absence of krypton from the high-boiling portion was due to the fact that in order to prepare it they would have had to use 60,000 times the amount of air they actually used, and then again while metargon is a solid, at the temperature of liquid air, krypton is probably liquid, and therefore more volatile. Moreover, the air from which the krypton was obtained had been filtered and so was freed from metargon.

Professor Schuster called attention to the fact that the spectrum of metargon showed great similarity to the spectrum of carbon, not in a few lines only, but throughout the whole visible spectrum. He thinks this a strong point against the dissimilarity of the two substances, and is not willing to accept this new element without further evidence. He thinks the spectroscopic evidence would indicate the presence of a compound of carbon mixed with argon or an unknown substance. Ramsay acknowledged the justice of Schuster's claim as to the great similarity of the two spectra, but decided as a result of further experiment that there was no evidence of the presence of carbon. He found that the gas had the same spectrum even after being sparked for two hours with oxygen; that no carbonic oxide bands could be found when the gas, mixed with oxygen, was introduced into a vacuum-tube and that a mixture of carbon monoxide and argon, after being sparked with oxygen, showed no carbon lines or bands. In hundreds of cases they have removed traces of carbon compounds by increasing the intensity of the current; but this had no effect here.

Professor Dewar says he has failed to see any signs of metargon in a sample of pure argon, which Lord Rayleigh had given him, which had been repeatedly liquefied, and he inquires as to the absence of the metargon of Ramsay and Travers. We thus see that while the presence of krypton and neon are fairly well established, more evidence is desired with regard to metargon.

Professor Nasini of Padua has been engaged for some time on a study of the gases emanating from the earth in various parts of Italy, and has already published some of the results obtained. In a brief note communicated to the French Academy, in July, he announced the discovery of a gas which had not been found before on the earth.

The gases from the Solfatara di Pozzuoli contained a gas which gave the wave-length 531.5, corresponding to that of corona 1474 K, attributed to an undiscovered element coronium, which should be lighter than hydrogen. The fumarole of Vesuvius also gave a gas with the same characteristic lines which are approximately those of various elements as iron and potassium; but these elements could not be present in the gas used. One of the lines is very near one of the nitrogen lines; but it cannot be due to nitrogen, as the other lines are not present. This gas to which the name coronium has been given was observed in the corona of the sun and was erroneously supposed, for a long time, to be present in the aurora borealis. It is lighter than hydrogen and cannot be a modification of any known element as it occurs at a distance of 300,000 miles from the body of the sun, and the lines are perfectly sharp and straight and never bent, as are those of all known elements, during solar disturbances.

The appearance of so many new elements at one time will no doubt prove embarrassing with the present arrangement of the Periodic System, and attempts will probably be made to rearrange the system to conform to these new discoveries. Professor Crookes has suggested an arrangement of the elements in the form of a double spiral in which the elements are arranged in three dimensions in space, the three elements discovered by Ramsay falling in the vertical column under helium between the hydrogen family, containing chlorine, bromine and iodine, and the lithium family. J. E. G.

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## *Fermentation without Cells.*

Eduard Buchner delivered a lecture on this subject before the German Chemical Society, March 14, 1898, and an abstract of the lecture was published in the *Berichte*, April 25, 1898. In view of the importance of the results reached and described by Buchner, a brief account of the work is here given.

As is well known the investigations of Pasteur led to the conclusion that the process of fermentation necessarily involves the action of organisms. Pasteur regarded fermentation as a physiological act, closely and inseparably connected with the vital phenomena of the yeast cells. Other investigators, on the contrary, as Moritz, Traube, Berthelot, Liebig, and Hoppe-Seyler, were of the opinion that the yeast produces a substance which effects fermentation just as it produces a definite chemical substance, an unorganized ferment or enzyme, *invertase*, which splits cane-sugar into grape-sugar and fruit sugar. But this theory lacked experimental basis. The vitalistic theory of Pasteur, therefore, prevailed.

Buchner, in October, 1896, first obtained evidence that fermentation can be effected without cells, but doubted his results. Further work showed, however, that a liquid free from cells can be expressed from yeast which liquid can cause the fermentation of sugar.

The process by which the liquid is obtained is the following:

Fresh Munich low-fermentation beer press-yeast, dehydrated under a pressure of 50 atmospheres, is mixed with its own weight of quartz sand and a fifth of its weight of infusorial earth, and then thoroughly triturated. The process is interrupted only when the mass, which at first forms a dry powder, of itself becomes moist. Now, the dough-like mass, wrapped in a cloth, is subjected to a pressure of 500 atmospheres. In about two hours the cake is broken up, moistened with water, and again subjected to the same high pressure. From 1 kilogram yeast about 500 cc. liquid is obtained, and of this 140 cc. is water that has been added. The liquid from the press is allowed to drop directly upon a fluted filter and is collected in a vessel cooled to 0° by ice-water in order, as far as possible, to prevent any change of the liquid during the preparation.

The fresh yeast juice is a yellowish liquid, which appears almost clear by transmitted light, but is otherwise opalescent. It has a pleasant odor of yeast, and contains much carbon dioxide in solution. A considerable quantity of coagulable albumin is present in it. Enzymes are also present in the yeast juice. Of these, invertase has been identified. The presence of maltase and of a ferment capable of hydrolyzing glycogen appears probable. Proteolytic enzymes have been found in the juice by M. Hahn.

The most interesting property of the yeast juice, however, is its power to cause the alcoholic fermentation of sugars. Like yeast itself, it affects cane, malt, grape, and fruit sugars, but not lactose and mannite.

From all the numerous experiments that have thus far been made, the conclusion is drawn that the living yeast cells are not necessary to the process of alcoholic fermentation. The phenomenon of fermentation is not, therefore, to be regarded as a physiological act. It is rather brought about by an enzyme-like substance, *zymase*, which is only formed in nature in the living yeast cell. This substance cannot yet be isolated, on account of its instability, and the presence of other enzymes.

Buchner takes up the objections that have been raised against his conclusions, but makes it appear clear that these are not justified. I. R.